

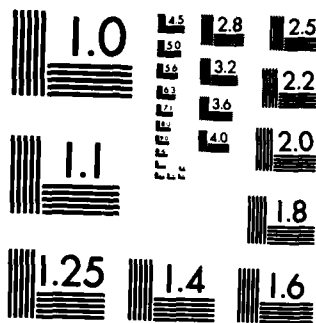
REAL-TIME FLUORESCENCE ANALYSIS OF THE CONTROLLED
INCINERATION OF ARMY CO. (U) NAVAL WEAPONS CENTER CHINA
LAKE CA R T LODA ET AL. DEC 84 NWC-TP-6559
SBI-AD-E900 431 F/G 19/1

UNCLASSIFIED

F/G 19/1

NL

END



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

ATC 200431

(2)

NWC TP 6559

Real-Time Fluorescence Analysis of the Controlled Incineration of Army Colored Smoke Compositions

AD-A152 479

by
Richard T. Loda
and
Timothy P. Parr
Research Department

DECEMBER 1984

NAVAL WEAPONS CENTER
CHINA LAKE, CA 93555-6001



DTIC
ELECTE
APR 16 1985
S B D

Approved for public release;
distribution is unlimited.

DTIC FILE COPY

00 4 10 107

Naval Weapons Center

AN ACTIVITY OF THE NAVAL MATERIAL COMMAND

FOREWORD

Polynuclear aromatic hydrocarbons can be produced during the thermal destruction of unserviceable colored smoke compositions. Because some of these compounds are carcinogenic, there is a need to monitor their possible release into the environment. The real-time monitoring of stack gases during the incineration testing of several Army colored smoke formulations is the subject of this report.

The work described herein took place in April 1984. The work was performed under the sponsorship of G. Zajicek of the Army Armament Material Readiness Command, Program Element No. 63721N, Task Area 50400 and Work Unit 138567.

This work has been reviewed for technical accuracy by E. D. Erickson and C. E. Dinerman.

Approved by:
E. B. ROYCE, Head
Research Department
20 November 1984

Under authority of
K. A. DICKERSON
Capt., USN
Commander

Released for publication by
B. W. HAYS
Technical Director

NWC Technical Publication 6559

Published by Technical Information Department
Collation Cover, 41 leaves
First printing 150 copies

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NWC TP 6559	2. GOVT ACCESSION NO. ADA152479	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) REAL-TIME FLUORESCENCE ANALYSIS OF THE CONTROLLED INCINERATION OF ARMY COLORED SMOKE COMPOSITIONS		5. TYPE OF REPORT & PERIOD COVERED Final April-June 1984
7. AUTHOR(s) Richard T. Loda and Timothy P. Parr		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Weapons Center China Lake, CA 93555-6001		8. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Weapons Center China Lake, CA 93555-6001		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS PE 62765N & 63721N, Task Area WF65559 & 50400, Work Unit 138567
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE December 1984
		13. NUMBER OF PAGES 80
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Colored Smoke Compositions Polynuclear Aromatic Hydrocarbons (PAHs) Combustion Products Real-time Fluorescence Spectroscopy Incineration		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See back of form.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 68 IS OBSOLETE
S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(U) Real-Time Fluorescence Analysis of the Controlled Incineration of Army Colored Smoke Compositions, by Richard T. Loda and Timothy P. Parr. China Lake, Calif., Naval Weapons Center, December 1984. 80 pp. (NWC TP 6559, publication UNCLASSIFIED.)

(U) This publication describes the use of a real-time, fluorescence-based polynuclear aromatic hydrocarbon (PAH) monitor and calibration system during the incineration testing of Army colored smoke compositions at the Los Alamos National Laboratory Controlled Air Incinerator facility. During these tests, no PAHs were found to be present in the incinerator effluent gases at a concentration level 1 ppm (the approximate gas-phase detection limit of the monitor). A fluorescence signal was observed, to varying degrees, with most of the smoke formulations, and its intensity appeared to track the NO_x monitor signal readings. It is hypothesized that the presence of NO in the system is sensitizing the emission of another, non-PAH material.

(U) To demonstrate the flexibility of the monitor system, a rudimentary analysis of some of the sump water collected during the incineration tests was also performed.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

CONTENTS

Introduction	3
Experimental	3
Materials	3
LANL Incinerator Complex	4
PAH Monitor Flow System	5
Results and Discussion	5
Preliminary Observations	5
Violet Smoke IV	6
Red Smoke III	7
Green Smoke IV	7
Yellow Smoke VI	8
Green Smoke VII and Nitric Oxide	8
Yellow Smoke XII	9
White Smoke I	9
Napthalene Calibration and Gas Combustion	10
Smoke Formulation Mixture	10
Sump Water Samples	10
Conclusions	11
References	14
Figures	15
Appendix A. Ingredients and Specifications of Army Colored Smoke Compositions	71

DTIC
ELECTE
S **D**
APR 16 1985
B



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

INTRODUCTION

The Naval Weapons Center's (NWC) design for a real-time monitor system to detect polynuclear aromatic hydrocarbons (PAHs) in combustion products has been described previously (Reference 1). In that work, the monitor system was put on-line during the incineration testing of a series of unserviceable Navy colored smoke compositions. These tests were performed at the Los Alamos National Laboratory (LANL) Controlled Air Incinerator (CAI) facility, Los Alamos, N. Mex., (Reference 2) in September 1983.

It was expected that the problems associated with the environmentally-safe incineration of Army colored smoke compositions would be similar to those encountered in the incineration of their Navy counterparts. Therefore, the NWC was contracted by the Army Armament Command, Rock Island, Illinois, to monitor the stack gas emissions produced during the incineration of Army colored smokes.

This report describes the PAH monitor results obtained from the Army colored smoke composition incineration tests that took place at the LANL in April 1984. During these tests, no PAHs were found to be present in the incinerator effluent gases at a concentration level ≥ 1 part per million (ppm) (the approximate gas-phase detection limit of the monitor). Since the monitor system has been discussed in great detail elsewhere (Reference 1), only the changes made from the Navy test configuration are covered here. The results are presented in chronological order, and they are broken down according to the LANL test feed schedule (Reference 3).

EXPERIMENTAL

MATERIALS

The naphthalene used in the calibration cell was purchased from Matheson, Coleman and Bell, Norwood, Ohio. It was used without further purification, after determining that its melting point range was 80-82°C.

The ingredients and specifications of the Army colored smoke compositions tested are given in Appendix A. The LANL test feed schedule (Reference 3) is given in Table 1, along with the proper names of the organic dyes which are used in each of the smoke formulations. Their chemical structures are shown in Figure 1. It should be noted that a number of these same dyes are also used in the Navy formulations (References 4 and 5).

TABLE 1. CS-2 Test Feed Schedule.

Phase no.	Feed material	Dyes
1	None	None
2	Violet Smoke IV	1,4 diamino-2,3-dihydroanthraquinone 1-methylaminoanthraquinone
3	Red Smoke III	1-methylaminoanthraquinone
4	Green Smoke IV	Dibenzo(a,h)pyrene-7,14-dione 1,4-di-p-toluidinoanthraquinone Benzanthrone
5	Yellow Smoke VI	Dibenzo(a,h)pyrene-7,14-dione Benzanthrone
6	Green Smoke VII ^a	2-(2'-quinolyl)-1,3-indandione 1,4-di-p-toluidinoanthraquinone
7	Yellow Smoke XII ^a	2-(2'-quinolyl)-1,3-indandione
8	White Smoke I	None
9	None	None

^aSmoke formulations using sugar (lactose) in place of sulphur as the reducing agent.

LANL INCINERATOR COMPLEX

The Los Alamos CAI used for the incineration testing of the colored smoke compositions has been described elsewhere (Reference 2). For our purposes, the relationship of the PAH monitor sampling location to the rest of the system is of primary importance. A block diagram of the CAI is given in Figure 2. The PAH monitor sampling location ($T < 93.3^{\circ}\text{C}$) is between the two high-efficiency particulate air (HEPA) filter assemblies, just before the Demister Outlet (DO) sampling location.

PAH MONITOR FLOW SYSTEM

The PAH monitor flow system that was used in the incineration testing of the Navy colored smoke formulations (Reference 1) is given in Figure 3. The stack gases from the PAH monitor sampling location passed through heated and insulated lines (1 and 2) before reaching the fluorescence flow cell, mounted in the Spex Industries instrument. A calibration cell was also teed into line 2 so that the instrument response to a known PAH concentration could be measured. The line running parallel to line 2 in the figure was necessary to prevent the condensation of the calibration PAH in the lines during the on-line sampling of the stack gases.

Before our arrival at the LANL for the Army tests, the PAH monitor system had been moved to an air-conditioned room to provide a less hostile environment for the instrument. Sampling lines had been run from the PAH monitor sampling point up to the air-conditioned room. The sampling line length for this test was 29.5 feet, compared to the 11-foot line used during the Navy test. Figure 4 shows the valving system set up at the sampling point to allow for the sampling of either the stack gases, or room air from near the HEPAs. The room air, sampled through the same line used for the stack gases, provided a background measurement for comparison purposes.

For the work described in this report, the temperatures for lines 1 through 4 of Figure 3 were 79.4, 81.7, 78.9, and 71.7°C. The HEPA temperature (at the PAH monitor sampling location) was 73.9°C and the set point for the fluorescence flow cell was 79.4 ± 1.4°C.

RESULTS AND DISCUSSION

PRELIMINARY OBSERVATIONS

The fluorescence spectra presented in the following sections were all taken with an approximately 5 nm resolution for both excitation and emission. The wavelengths were scanned in the burst mode, at 1 nm/step, with a 1 second integration time. The fluorescent emission was detected perpendicular to the excitation beam. Temporal scans at fixed wavelengths were taken with a 1 second integration time. Data was acquired from either the sample photomultiplier alone (S1 mode), or with the ratio of the sample intensity to a reference photomultiplier (S1/S2 mode). The latter technique corrects the result for changes in the xenon lamp intensity as a function of wavelength. It also corrects for lamp intensity fluctuations with time.

Using the calibration cell, the monitor response to a 12.4 ppm concentration of naphthalene was measured as a calibration check. Because of the possibility of instrumental background contributions to the measurements, difference scans were recorded. Off-line (room air) data was subtracted from data taken on-line (stack gases). Excitation wavelengths, known to excite PAHs from previous work (Reference 1), were used in all cases.

VIOLET SMOKE IV

Prior to starting the feed for the Violet IV smoke, the monitor was put on-line while the incinerator system was burning only natural gas. The emission scan results are presented in Figure 5 and the difference plot is given in Figure 6. There is some weak emission near 318 nm when 277 nm excitation is used. It is unlikely that this signal is caused by the presence of a PAH since the emission is even bluer than that of naphthalene (emission maximum at 328 nm). The broad emission near 500 nm is instrumental background and the feature at 554 nm is second order 227 nm light.

A temporal scan is shown in Figure 7. The Violet IV smoke composition feed was started approximately 5200 seconds into the scan. Difference data are presented in Figures 8 and 9. These data are very similar to what was observed without the smoke formulation (Figures 5 and 6). Emission scans, measured using a series of excitation wavelengths known to excite PAHs, are presented in Figures 10 through 13. There is no definite evidence for the presence of PAHs (>1 ppm) in any of these data.

The LANL NO_x monitor had been registering approximately 180 ppm of NO_x during the Violet IV smoke incineration. An attempt to observe nitrogen dioxide (NO_2) emission from the stack gas is given in Figure 14. None was observed. This was not altogether unexpected since the predominant NO_x species present at the incinerator operating temperature (1010°C) is nitric oxide (NO) (Reference 6). An attempt to observe NO emission is shown in Figures 15 and 16, and the difference spectrum is given in Figure 17. The narrow features at 236, 248, 260, and 272 nm in Figure 17 are caused by the presence of NO in the stack gas. There is also a much broader emission with a maximum near 306 nm. This emission is stronger than the 318 nm emission observed earlier under 277 nm excitation. It is unlikely that the 306 nm emission was caused by the presence of a PAH at a concentration level ≥ 1 ppm since it is again, bluer than the emission of naphthalene.

A fluorescence excitation spectrum of the 360 nm emission is given in Figure 18. The NO molecule has a known absorption band at 226 nm (Reference 7). Since only weak NO emission is seen in Figure 17, it is

quite likely that the NO is sensitizing the species responsible for the 306 nm emission. In other words, upon photoexcitation, the NO in the stack gas transfers its excitation energy to an accepting species, which then emits. This would also explain why the 306 nm emission intensity appeared to be roughly proportional to the NO_x monitor concentration reading for all the smoke formulations.

Figures 19 through 22 are temporal scans measured during the incineration of the Violet IV smoke. The abrupt signal level changes in Figures 19 and 20 were caused by the switch from on-line to room air sampling during the scans. Some of the other signal spikes were observed to correlate with times that the sampling firm was inserting or removing their probes from the incinerator flow system.

RED SMOKE III

Figure 23 shows the result of a temporal scan taken during the switch from the Violet IV smoke to the Red III smoke incineration. There was no dramatic change in the 306 nm emission during the transition. As can be seen from the emission scans of Figures 24 through 30, the results are strikingly similar to those observed for the Violet IV smoke (compare to Figures 8 through 13 and 15). The 306 nm emission was observed, but there was no evidence for the presence of PAHs.

During the temporal scan shown in Figure 31, it was found that 20 to 30 mL of liquid water had made its way into the pump trap on the exit side of the fluorescence flow cell of the PAH monitor. The water had come from the sampling location through the flow lines. This is the reason for the dramatic increase in signal at the 460-second point in the figure. This water was collected and saved for later analysis. The increase in scattered light interference caused by the water problem can be seen by comparing the second order excitation peak in Figure 32 to its earlier counterpart (Figure 25). Nevertheless, there is still no evidence for PAHs.

Two final temporal scans taken during the incineration of the Red III smoke are given in Figures 33 and 34. The effect of stopping the smoke feed to the incinerator can be seen in Figure 34. Again, it should be noted that the 306 nm emission signal intensity appeared to be roughly proportional to the NO_x monitor concentration reading.

GREEN SMOKE IV

Figure 35 presents a temporal scan taken during the start of the incineration of the Green IV smoke. The liquid feed containing the green smoke was initiated 600 seconds into the scan. The 306 nm emission is about two to three times stronger for this smoke formulation

than for the previous ones (Violet IV and Red III). Although this formulation contains three separate dyes (Table I), the total dye concentration in the formulation is no greater than in the other formulations (see Appendix A). All three formulations studied thus far have dyes which contain the nitrogen atom. The increased 306 nm signal for the Green IV smoke does not appear to be related to the amount of nitrogen in the dyes themselves.

Fluorescence emission scans taken during the incineration of the Green IV smoke are given in Figures 36 and 37. The burner went out during the scan of Figure 37. Figures 38 and 39 are temporal scans obtained during the restart of the liquid feed (Green IV smoke) to the burner.

Figures 40 through 53 present a series of scans taken through the rest of the Green IV smoke incineration. For this test, as with the last two, no PAHs were seen. The 302-306 nm emission,* which appears to track with the NO concentration, was the only thing observed.

YELLOW SMOKE VI

Figures 54 through 62 represent scans taken during the incineration of the Yellow VI smoke. The 302 nm emission intensity for this formulation was similar to that observed for the Violet IV and Red III smokes, but weaker than that observed for the Green IV smoke. As a point of interest, this smoke formulation does not contain any dyes with a nitrogen atom in the dye molecules. As with the previous tests, no PAHs were found to be present during the incineration of this smoke formulation.

GREEN SMOKE VII AND NITRIC OXIDE

The Green VII smoke was the first of two sugar-based, rather than sulphur-based formulations tested (see Table 1). Figures 63 and 64 present temporal scans taken during the incineration changeover period from the Yellow VI smoke to the Green VII smoke. The Green VII smoke feed was started at 2450 seconds in the scan of Figure 63. The 302 nm emission intensity for this material was greater than that observed for Violet IV, Red III, or Yellow VI smokes but similar to that obtained for the Green IV smoke. This may mean that the 302 nm emission could be related to the presence, or decomposition of, the 1,4-dip-toluidinoanthraquinone dye. The fact that the 302 nm emission was

*Because of the broad nature of this emission, it is felt that the same species is being observed, whether monitoring at 302 or 306 nm. Both values will be seen in the figures.

strong for this sugar-based formulation would imply that the presence of sulphur in the smoke is not responsible for the emitting species.

A tank of NO in nitrogen was temporarily connected to the room air inlet (Figure 4) and the PAH monitor response to the NO in nitrogen was measured. The fluorescence emission and excitation spectra of 244 ppm of NO in nitrogen are given in Figures 65 and 66. The structured emission matches the narrow features present in the 302 nm emission spectrum of Figure 17, and it is quite clear that the 302 nm emission was not from NO alone. The excitation maximum of NO in nitrogen is 226.5 nm and it is approximately three times narrower than the 226 nm excitation feature measured for the 302 nm emission (compare Figures 66 and 18). This may be caused by the presence of another species, or possibly by the NO sensitization phenomenon discussed earlier. As a final point here, one must be cautioned against the direct comparison of the intensity values in Figures 17, 18, 65, and 66. The presence of oxygen in the stack gases (Figures 17 and 18) would cause a quenching of the NO emission, relative to that in a nitrogen atmosphere (Figures 65 and 66).

A number of additional scans taken during the incineration of the Green VII smoke are given in Figures 67 through 72. Once again, there was no evidence for the presence of PAHs. The 302 nm emission, which appears to track the NO concentration, was the only significant finding.

YELLOW SMOKE XII

The Yellow XII smoke was the second of the sugar-based formulations tested (Table 1). Figures 73 and 74 present temporal scans taken during the incineration changeover period from the Green VII smoke to the Yellow XII smoke. The Yellow XII smoke feed was started at 1460 seconds in the scan of Figure 73. As can be seen from Figure 73, the 302 nm emission intensity for this material was at least a factor of 10 lower than any of the other smoke formulations tested to this point. Additional scans for the Yellow XII smoke formulation are given in Figures 75 through 83. Once again, there was no evidence for the presence of PAHs. For that matter, in two of the scans (Figures 79 and 83), there was no change in the signal level for the 302 nm emission when the system was switched off-line to monitor room air.

WHITE SMOKE I

The White I smoke was the only formulation that did not contain any dye (Table 1). The scans taken during the incineration of this material are presented in Figures 84 through 100. As can be seen from the figures, almost no emission was seen for any of the scans.

NAPHTHALENE CALIBRATION AND GAS COMBUSTION

To ensure that the PAH monitor system was still functioning properly, naphthalene was put into the diffusion cell, and the instrument response was measured. The results are shown in Figure 101, where it can be seen that signal intensity decreases by a factor of two when the flow rate is increased by a factor of two. The concentrations for naphthalene were 12.4 and 6.2 ppm, respectively. The reader should also be reminded that naphthalene is one of the more difficult PAHs for the monitor to detect (i.e., other PAHs would give a larger signal for an equivalent concentration) (Reference 1).

The monitor was next put on-line while only natural gas was being burned (no liquid feed). The wavelengths were set for the detection of NO in the stack gases. The NO_x monitor was reading 34 ppm at the time.

A temporal scan is shown in Figure 102. From Figures 65 and 66 we have that 244 ppm of NO should give 5000 counts in the absence of oxygen. For 34 ppm of NO one should therefore see $(5000/244) \times 34 = 696.7$ counts. Approximately 7 counts are observed for 34 ppm of NO in air from Figure 102. This factor of 100 for the oxygen quenching of NO is in good agreement with the literature (Reference 8). Additional emission scans, with different excitation wavelengths were measured during the gas burn, but no other emission was observed.

SMOKE FORMULATION MIXTURE

As a final smoke incineration test, all of the material remaining from the previous runs were mixed together into a conglomerate sample. Scans taken during the incineration of this mixture are given in Figures 103 and 104. From the figures it can be seen that the same kind of emission was obtained for this mixture as that obtained for the individual formulations.

SUMP WATER SAMPLES

Following the completion of the incineration tests, the fluorescence flow cell assembly was removed from the PAH monitor and the sample chamber was cooled to room temperature (23°C). To demonstrate the flexibility of the fluorimeter, it was decided to use the instrument at room temperature, with a standard cuvette, to examine some of the water samples collected during the tests. Three samples were studied in the limited time allotted for these room temperature analyses. The first was a sample of quench tower sump water, collected following the Red III smoke incineration test. The second was a sample of the absorber tower sump water, collected following the Red III smoke incineration test, and the last was a sample of the water that was collected from the pump trap in the PAH monitor flow system during the whole series of tests. Visibly, all three fluoresced blue-violet under ultraviolet (UV) excitation.

Excitation-emission matrix (References 1 and 9) data on the quench sump and absorber tower sump water samples are given in Figures 105 and 106. Essentially, this data consists of a series of emission spectra, taken over a series of excitation wavelengths. The vertical axis is the intensity of the emission. There are a number of things to note about these data. The strongest spectral feature in both figures represents the scattered radiation from the excitation source. It is most intense when the excitation wavelength value equals the emission wavelength value (Rayleigh scattering). This scattering signal forms the intense diagonal line across the excitation-emission matrix. All the fluorescence from the sample lies on or below this line. The fact that the Rayleigh scattering is so intense in these figures implies the presence of particulates in the water samples. There is a second, weaker diagonal line that runs approximately parallel to the Rayleigh scattering line in both figures. This is caused by Raman scattering of the water. From Figure 105 it can be seen that the emission spectra (horizontal lines) change with a change in the excitation wavelength. This is clear evidence for the presence of a multicomponent mixture. For a single species, the emission spectrum should change only in intensity, not wavelength, as the excitation wavelength is varied.

It is interesting to note that the components responsible for the bluest emission in the quench sump water do not make it through the system to the absorber tower (compare Figures 105 and 106, remembering that the Rayleigh and Raman scattering features are in both figures). The selective emission and excitation of the reddest component of the mixture are presented in Figures 107 and 108. In this case the observations were of the pump trap water, but it would appear that this component makes its way in the incinerator system at least as far as the PAH sampling location (see Figure 2).

Time constraints prevented further analysis of the water samples, but these rudimentary results are presented here mainly to demonstrate the additional capabilities of the monitor system as an analytical tool. As a final note on this topic, it should be realized that the potential sensitivity of this system for fluorescing liquid samples could be approximately 10,000 times greater than the sensitivity for gas phase samples. This is because the sample density is approximately 1000 times larger in the liquid, and the air (oxygen) quenching would be less severe in the liquid phase.

CONCLUSIONS

A number of Army colored smoke compositions were incineration tested at the LANL CAI facility. A monitor analyzed the incinerator effluent for environmentally hazardous PAH materials during the tests.

At the sampling location, no PAHs were detected (on a ≥ 1 ppm level) during the incineration of any of the smoke compositions studied. This was true for all the incinerator conditions used, over the approximately 4 days of testing. A signal was observed (emission maximum 302 nm, excitation maximum 226 nm) which occurred to varying degrees with most of the smokes. The intensity of this signal appeared to follow the NO_x monitor signal intensity, and 226 nm is, in fact, a spectral region over which NO absorbs. It is suspected that the NO present in the system is being excited at 226 nm and then transferring its excitation energy to compound(s) X, which emit(s) at 302 nm. The fact that only weak NO emission is observed is in agreement with this hypothesis.

The 302 nm emission of compound(s) X is bluer than any of the target PAHs known to be formed from the incomplete combustion of the smoke materials (Reference 1). A survey of cataloged spectra (Reference 10) revealed that the only PAH that might emit near 302 nm is fluorene, but if it were present, it is not clear why there was no absorption near 260 nm. It is, therefore, highly unlikely that the 302 nm emission was coming from a PAH. It is interesting to note that very little signal of any kind was observed for the White I smoke (which contains no dye), and for the Yellow XII smoke (one of the sugar-based, rather than sulphur based formulations). However, the presence of the 302 nm emission for the Green VII smoke (sugar-based) would argue that the presence of sulphur in the formulation is not responsible for the emitting species.

On several occasions during the tests, liquid water made its way through the flow line/fluorescence cell and wound up in the pump trap. This caused a dramatic increase in scattered light interference and may have caused some fluorescence cell contamination. A possible solution to this problem would be to have the sampling lines come off the top of the flow system, rather than the bottom, where water can collect.

Following the smoke tests, the fluorescence flow cell was removed and visually inspected. There were a number of water spots on the cell, caused by the liquid water problem described above. The instrument response to a standard water Raman signal was checked. This was done because the calibration signal observed for naphthalene during these tests was about two times lower than during the Navy tests in September 1983. The water Raman signal was down by a factor of 1.6 compared to that obtained when the instrument was new. It is not clear why the instrument throughput seems to have degraded. It may be that the lamp is losing its brightness.

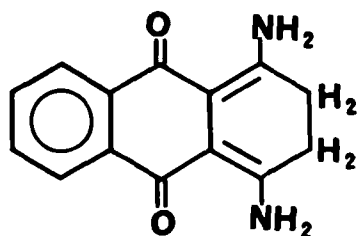
To demonstrate the flexibility of the fluorimeter, some of the water samples collected during the incineration tests were examined. Although a complete analysis was not undertaken, there is clear evidence that some, but not all of the water impurities were removed at the quench tower stage.

NWC TP 6559

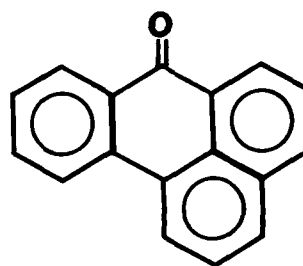
Finally, it should be mentioned that the air-conditioned room was much easier on the instrument (and the operators), and that on/off line difference scans should be used in the standard operating procedure for the monitor.

REFERENCES

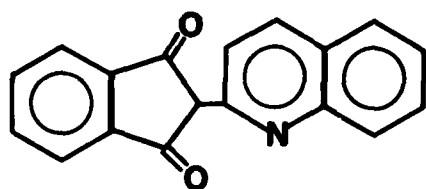
1. Naval Weapons Center. *The Design and Operation of a Real-Time Polynuclear Aromatic Hydrocarbon (PAH) Monitor for the Analysis of Combustion Products Formed in the Incineration of Navy Colored Smoke Compositions*, by R. T. Loda, Research Department. China Lake, Calif., NWC, in process. (NWC TP 6525, publication UNCLASSIFIED.)
2. Los Alamos National Laboratory. *The Los Alamos Controlled Air Incinerator for Radioactive Waste*, by R. A. Kronig, W. E. Draper, J. M. Newmeyer and C. L. Warner. Los Alamos, New Mexico, LANL, October 1982. (Waste Management Group H-7 Report No. LA-9427 Vols. I and II, publication UNCLASSIFIED.)
3. ----- . *Experimental Test Plan for CAI Test #17-CS-2*. Los Alamos, New Mexico, LANL, April 1984. (Waste Management Group H-7, publication UNCLASSIFIED.)
4. Naval Weapons Support Center. *Controlled Incineration of Navy Colored Smoke Compositions*, by Applied Sciences Department. Crane, Ind., NWSC, July 1978, 81 pp. (NWSC/CR/RDTR-86, publication UNCLASSIFIED.)
5. A. Chin and L. Borer. "Identification of Combustion Products from Colored Smokes Containing Organic Dyes." *Prop., Explo., Pyrotech.*, Vol. 8 (August 1983), pp. 112-118.
6. John N. Driscoll. *Flue Gas Monitoring Techniques*. Ann Arbor, Ann Arbor Science, 1974.
7. G. W. Bethke. "Oscillator Strengths in the Far Ultraviolet. I. Nitric Oxide." *J. Chem. Phys.*, Vol. 31, No. 3 (September 1959), pp. 662-668.
8. M. Birnbaum. "Laser-Excited Fluorescence Techniques in Air Pollution Monitoring," in *Modern Fluorescence Spectroscopy*, ed. by E. L. Wehry. New York, Plenum Press, 1976, Vol. 1, Chapter 5, pp. 121-157.
9. G. D. Christian, J. B. Callis and E. R. Davidson, "Array Detectors and Excitation-Emission Matrices in Multicomponent Analysis," in *Modern Fluorescence Spectroscopy*, ed. by E. L. Wehry. New York, Plenum Press, 1981, Vol. 4, Chapter 4, pp. 111-165.
10. I. B. Berlman. *Handbook of Fluorescence Spectra of Aromatic Molecules*. New York, Academic Press, 1971.



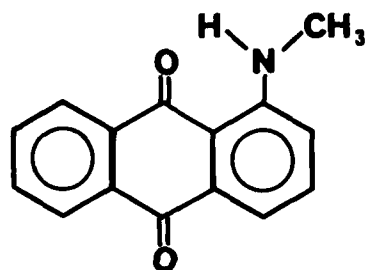
1,4-Diamino-2,3-dihydro-anthraquinone



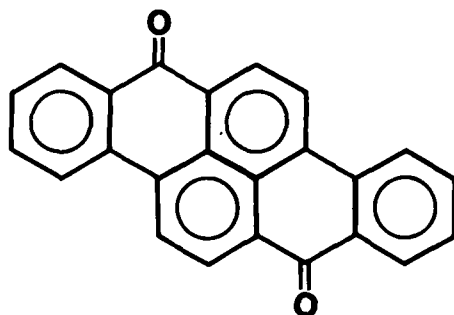
Benzanthrone or 7-oxo-7-benz(d,e)-anthraquinone



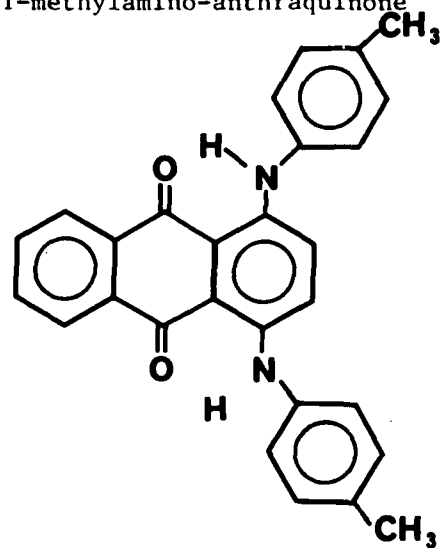
2-(2'-quinolyl)-1,3-indandione



1-methylamino-anthraquinone



Dibenzo(a,h)pyrene-7,14-dione



1-4-di-p-toluidino-anthraquinone

FIGURE 1. Organic Dyes Used in Smoke Formulations.

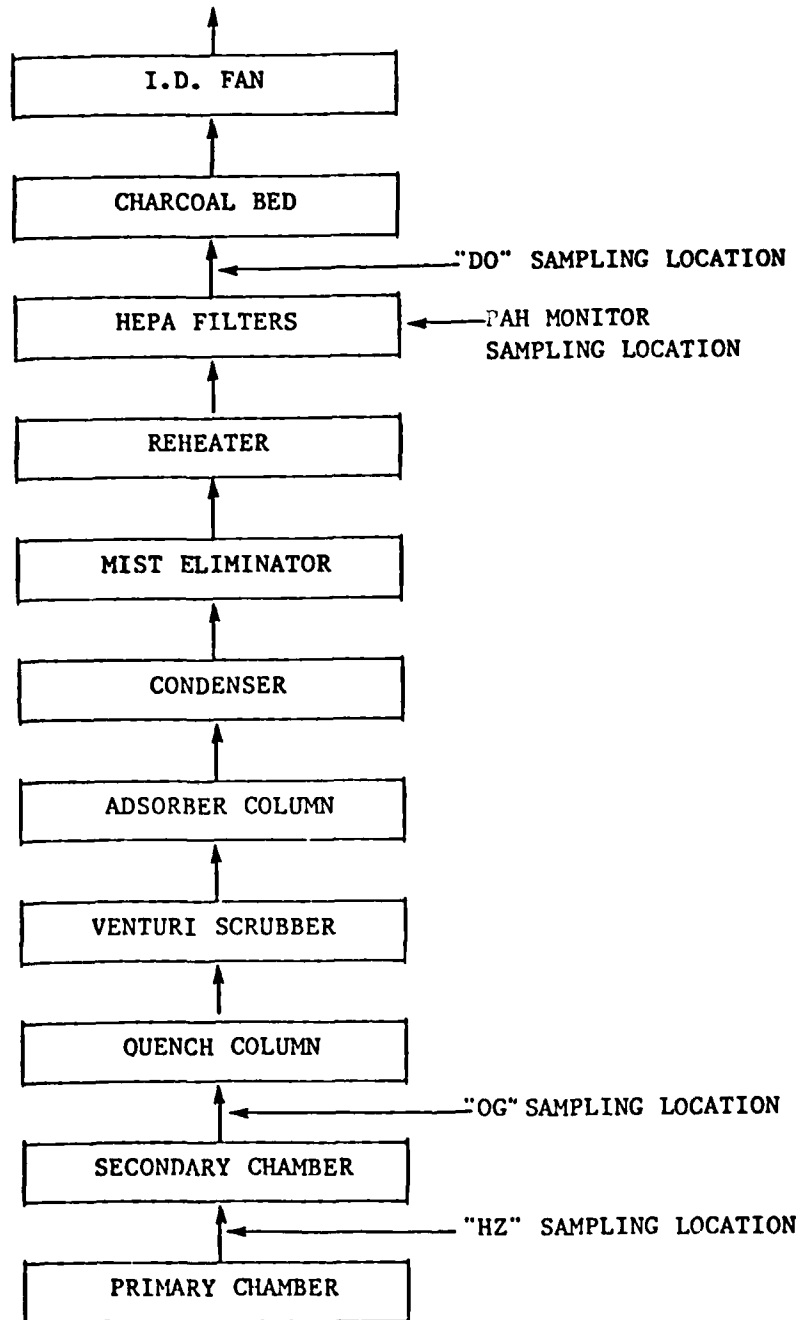


FIGURE 2. Incinerator Air Flow Schematic Showing Sampling Locations.

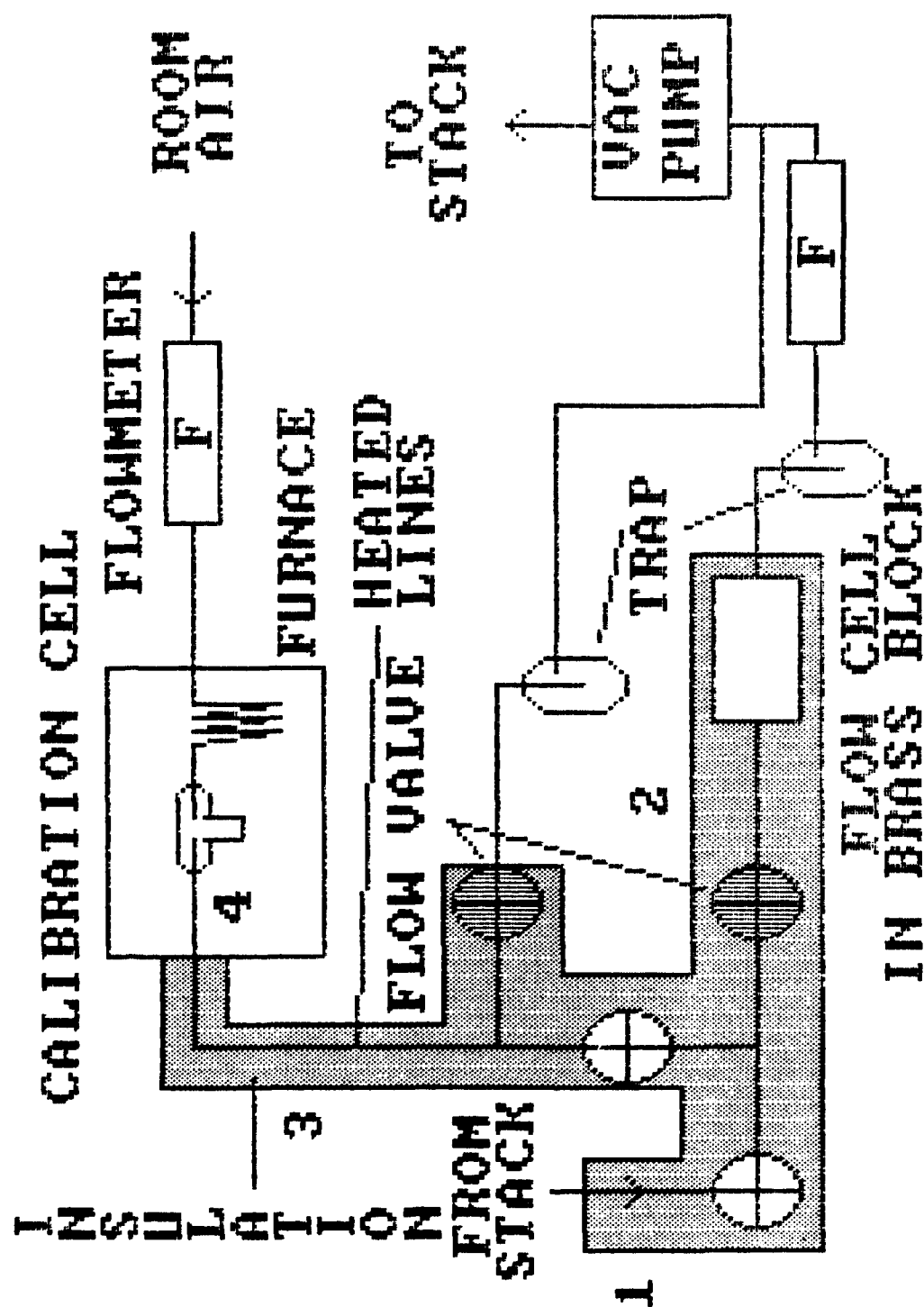


FIGURE 3. PAH Monitor Flow System.

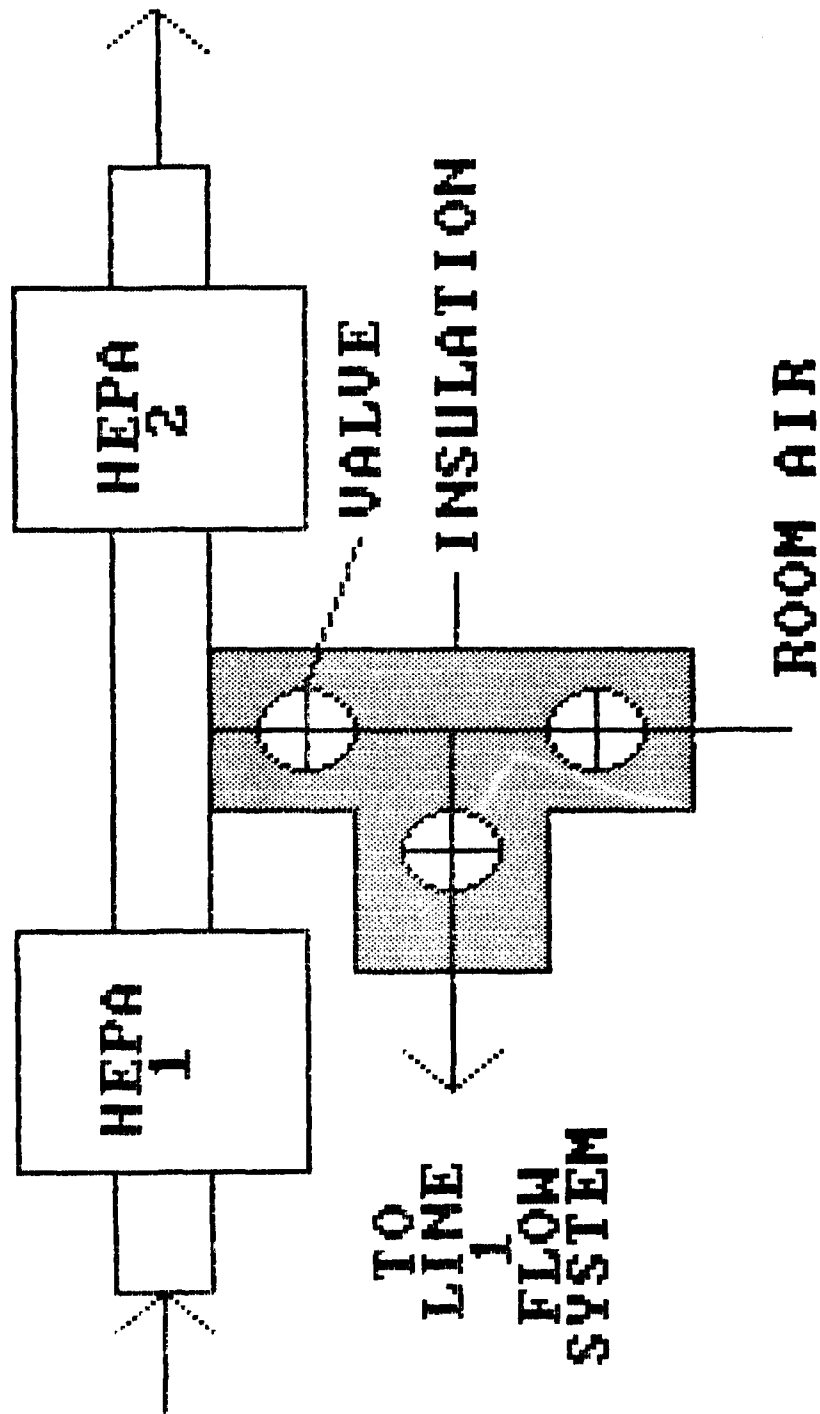


FIGURE 4. Valve System for Stack Gas and Room Air Sampling.

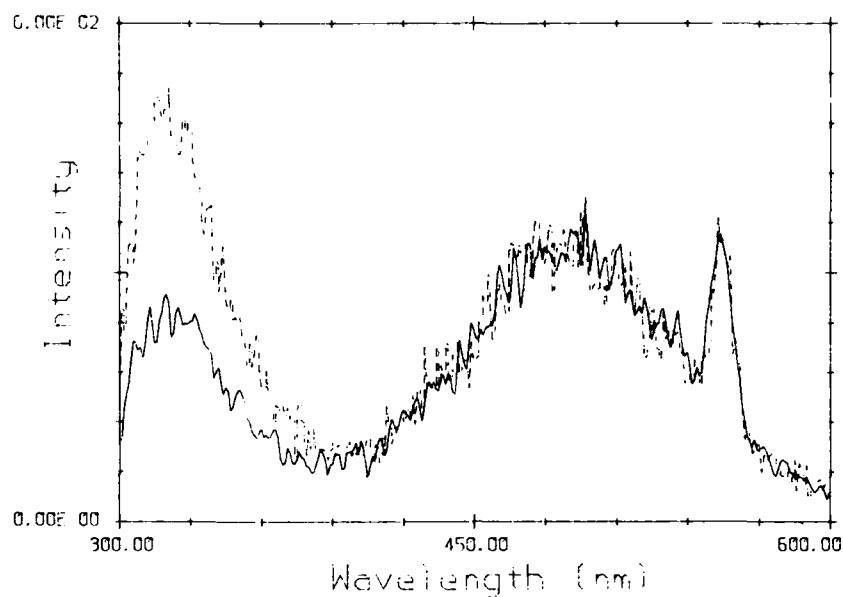


FIGURE 5. Fluorescence Emission Spectrum Started at 1352 on 25 April 1984. Only gas was being burned at the time. Ex = 277 nm, on-line (---), room air (—).

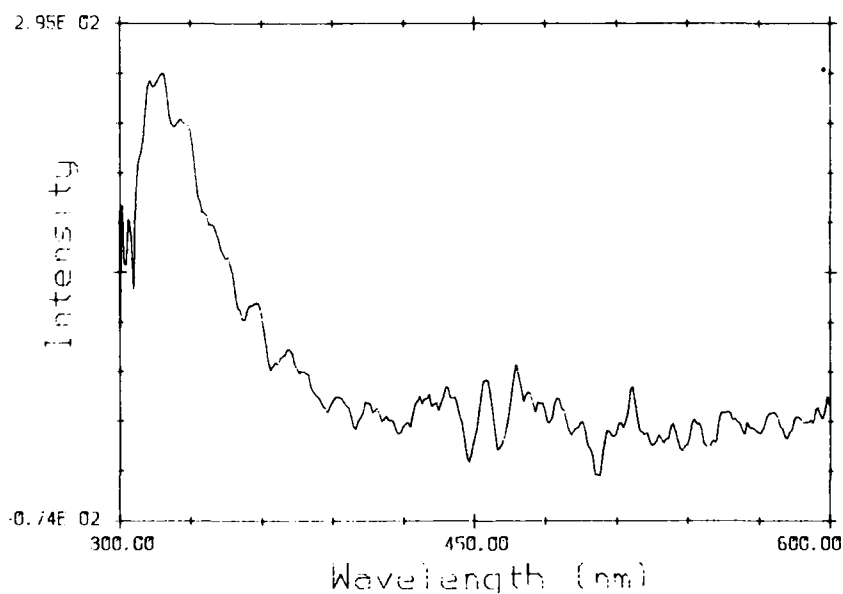


FIGURE 6. Difference Spectrum Obtained by Subtracting the Two Spectra in Figure 5.

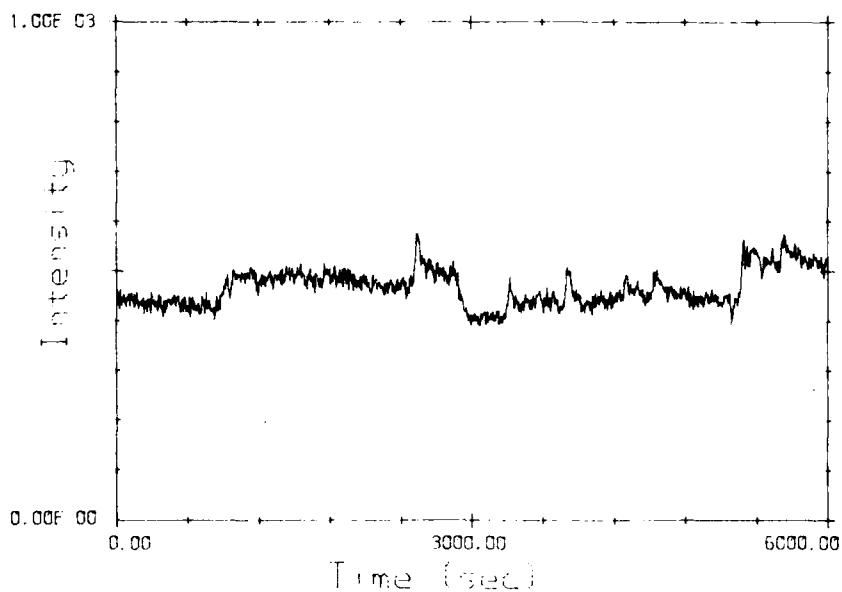


FIGURE 7. Temporal Scan Started at 1519 on 25 April 1984 During the Incineration of the Violet IV Smoke. The feed was started ~5200 seconds into the scan. Ex = 277 nm, EM = 318 nm.

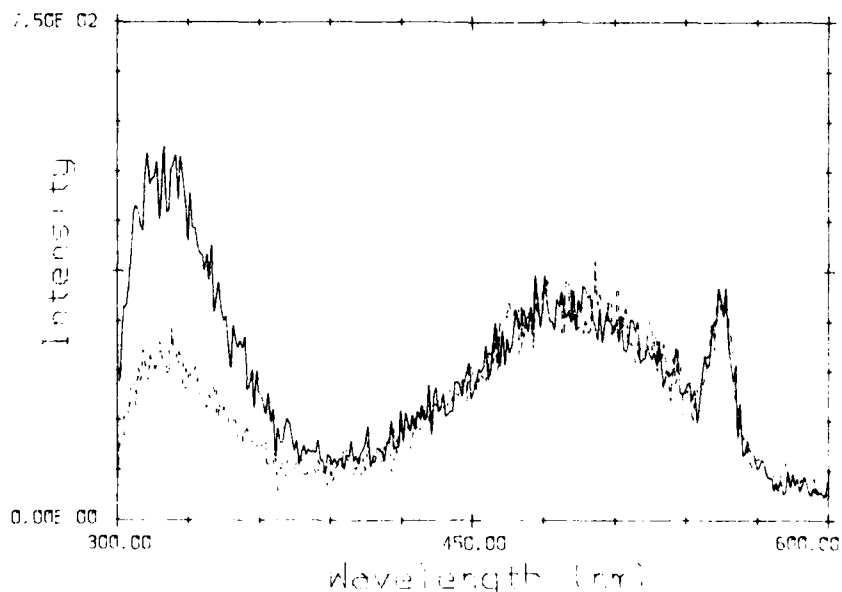


FIGURE 8. Fluorescence Emission Spectrum Started at 1702 on 25 April 1984 During the Incineration of the Violet IV Smoke. Ex = 277 nm, on-line (—), room air (---).

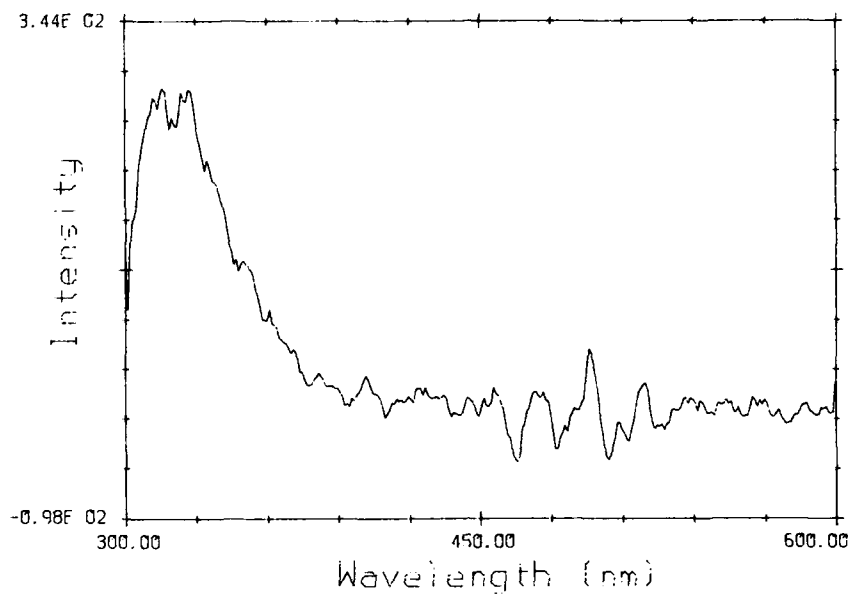


FIGURE 9. Difference Spectrum Obtained by Subtracting the Two Spectra in Figure 8.

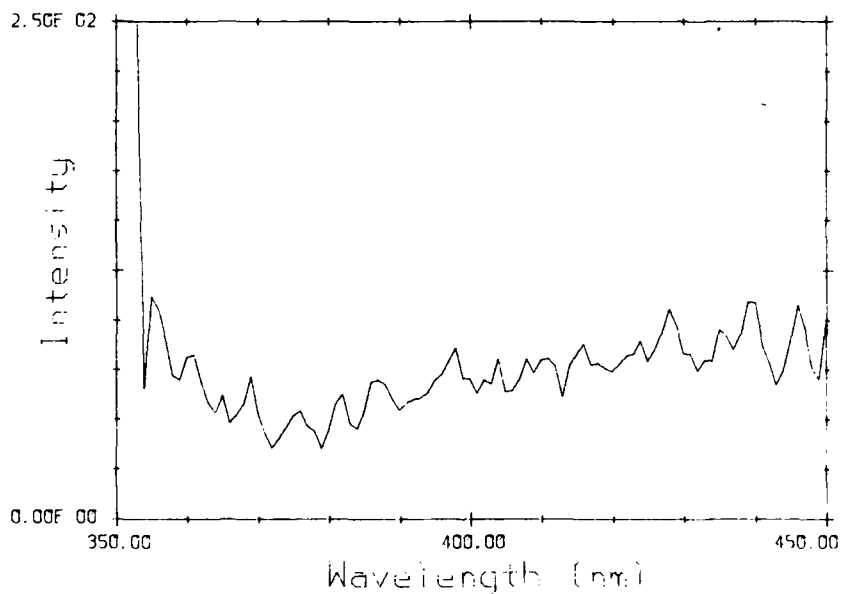


FIGURE 10. Fluorescence Emission Spectrum Started at 1745 on 25 April 1984 During the Incineration of the Violet IV Smoke. Ex = 344 nm. Excitation parameter for anthracene detection.

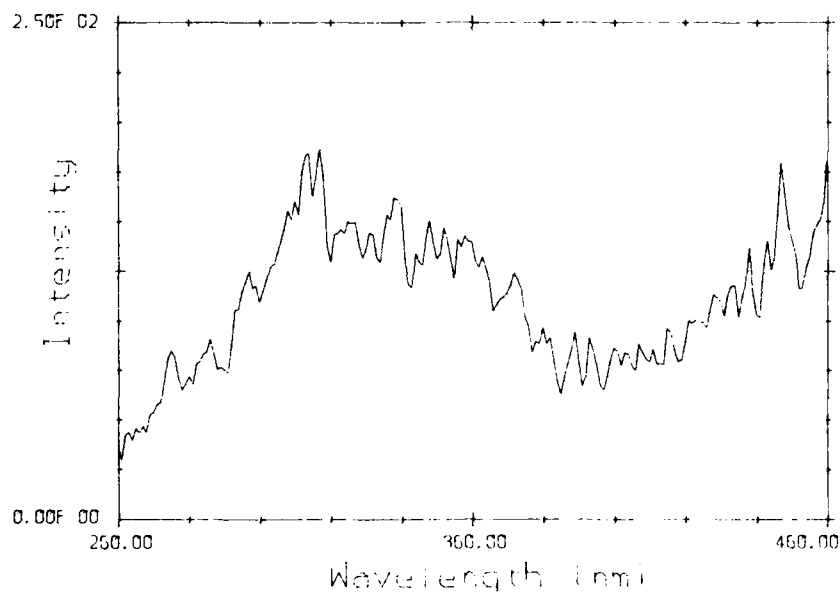


FIGURE 11. Fluorescence Emission Spectrum Started at 1754 on 25 April 1984 During the Incineration of the Violet IV Smoke. Ex = 240 nm.

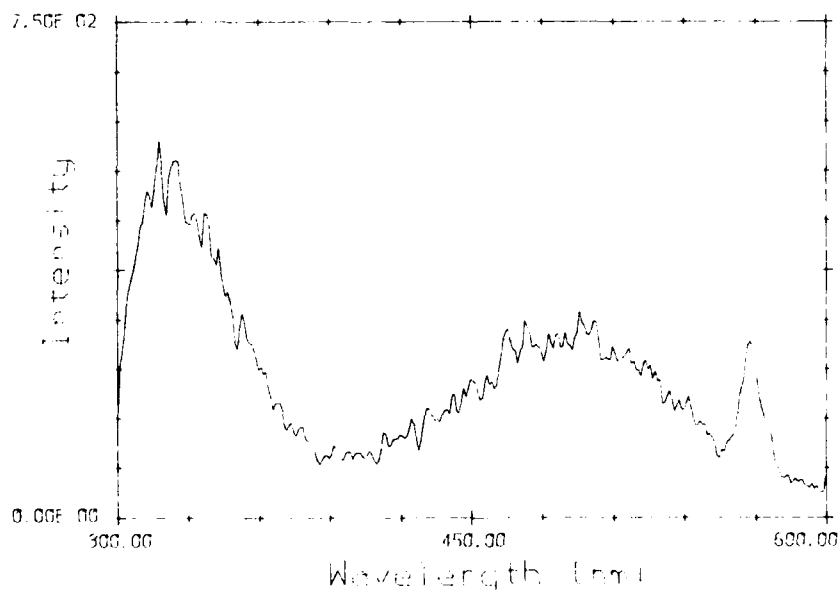


FIGURE 12. Fluorescence Emission Spectrum Started at 1800 on 25 April 1984 During the Incineration of the Violet IV Smoke. Ex = 284 nm. Excitation parameter for phenanthrene detection.

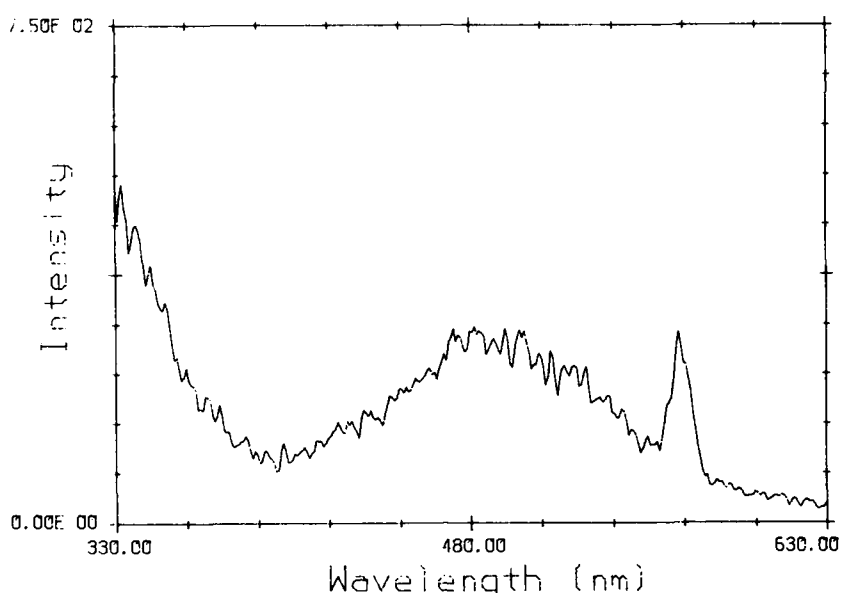


FIGURE 13. Fluorescence Emission Spectrum Started at 1812 on 25 April 1984 During the Incineration of the Violet IV Smoke. Ex = 310 nm.

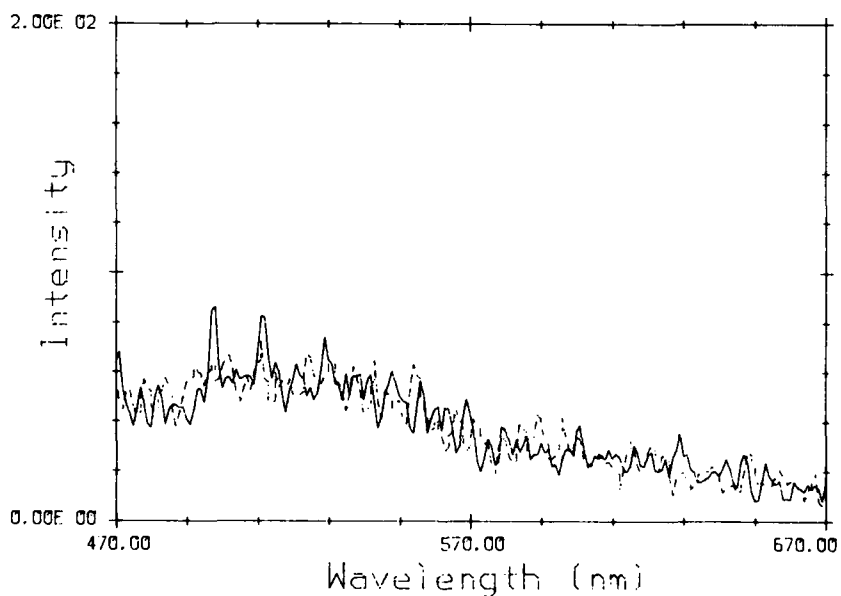


FIGURE 14. Fluorescence Emission Spectrum Started at 1910 on 25 April 1984 During the Incineration of the Violet IV Smoke. Ex = 450 nm. Excitation parameter for NO₂ detection.

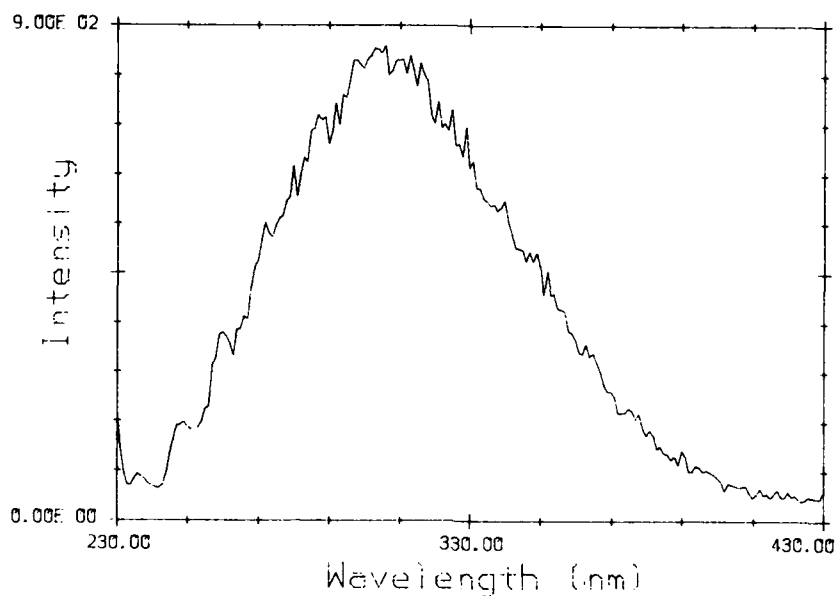


FIGURE 15. Fluorescence Emission Spectrum Started at 1936 on 25 April 1984 During the Incineration of the Violet IV Smoke. Ex = 226 nm. Excitation parameter for NO detection.

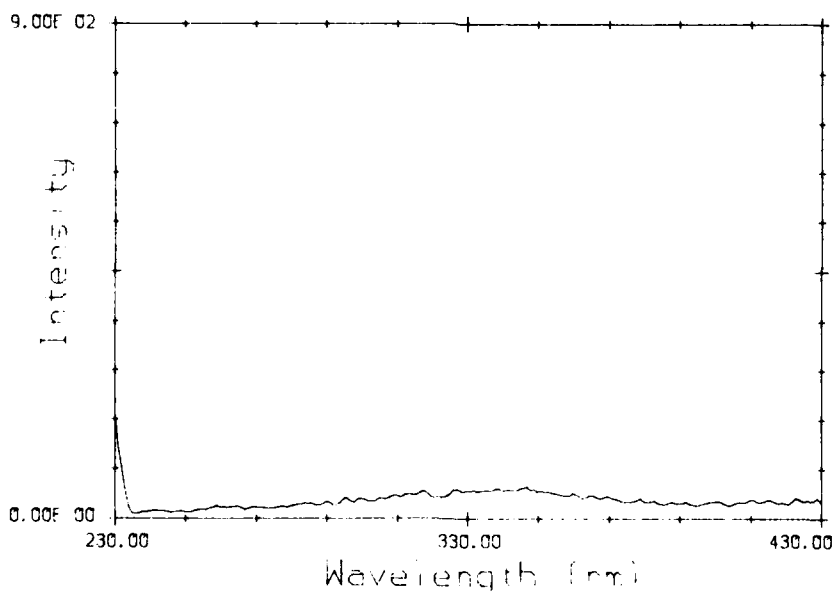


FIGURE 16. Fluorescence Emission Spectrum Started at 1958 on 25 April 1984 While Sampling Room Air. Ex = 226 nm.

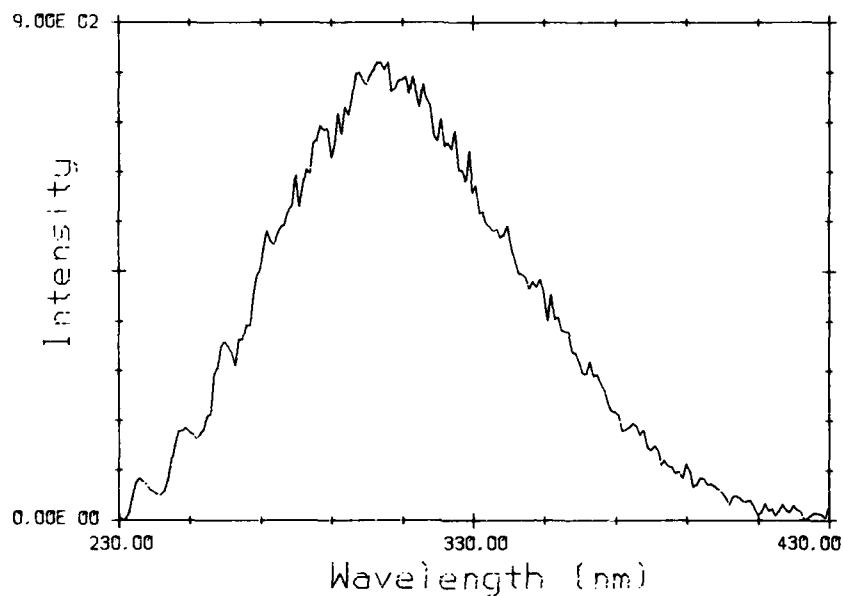


FIGURE 17. Difference Spectrum Obtained by Subtracting the Data in Figure 16 from the Data in Figure 15.

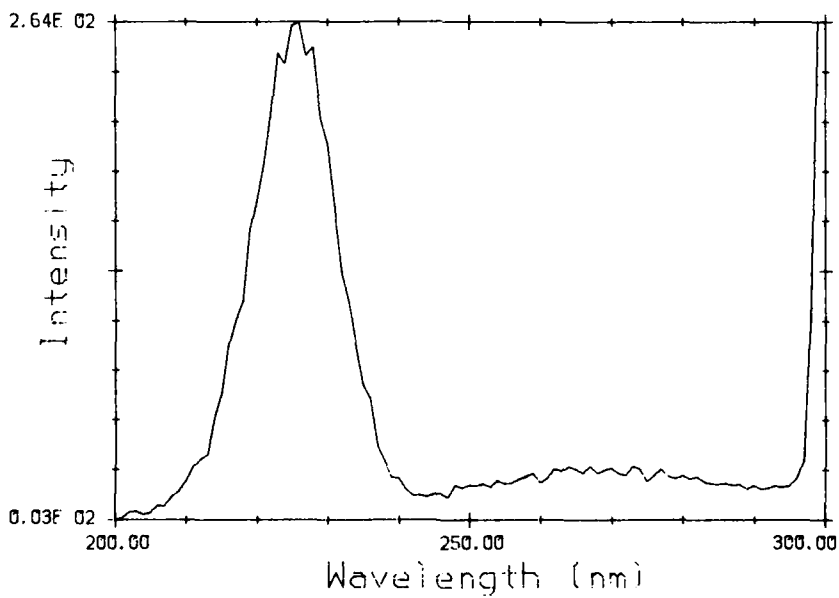


FIGURE 18. Fluorescence Excitation Spectrum Started at 2028 on 25 April 1984 During the Incineration of the Violet IV Smoke. $E_m = 306 \text{ nm}$, S1/S2 mode.

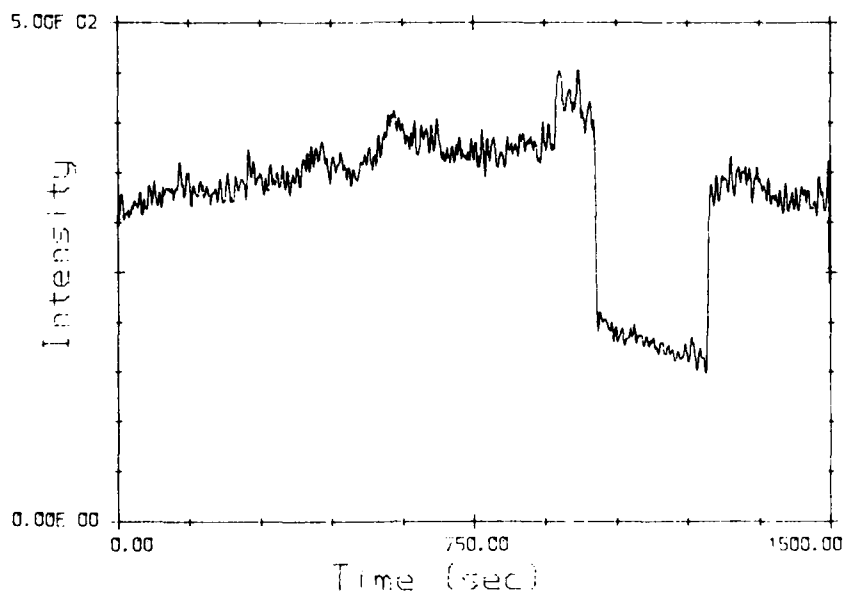


FIGURE 19. Temporal Scan Started at 2124 on 25 April 1984 During the Incineration of the Violet IV Smoke. Ex = 277 nm, Em = 318 nm. Switched to room air at 1000 seconds and back on-line at 1250 seconds.

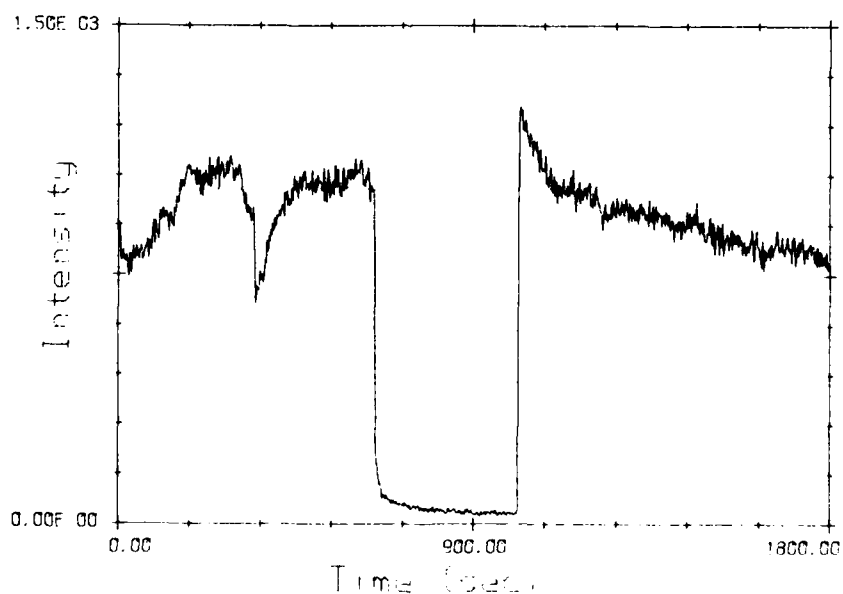


FIGURE 20. Temporal Scan Started at 2154 on 25 April 1984 During the Incineration of the Violet IV Smoke. EX = 226 nm, Em = 306 nm. Switched to room air at 650 seconds and back on-line at 1000 seconds.

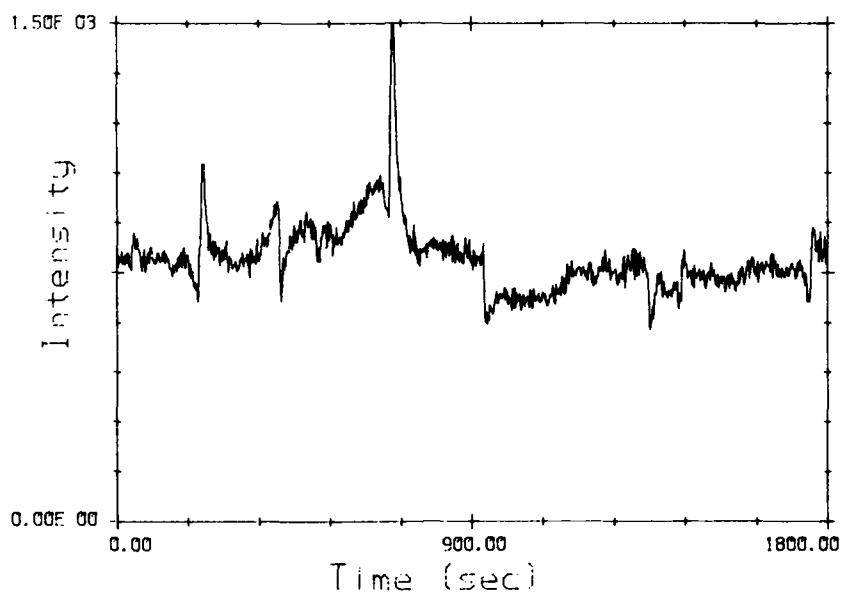


FIGURE 21. Temporal Scan Started at 2228 on 25 April 1984 During the Incineration of the Violet IV Smoke. Ex = 226 nm, Em = 306 nm.

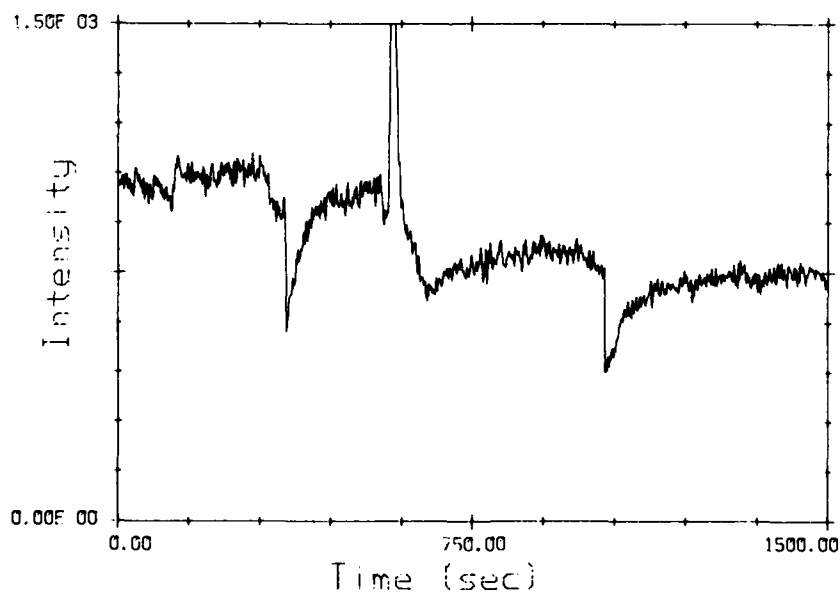


FIGURE 22. Temporal Scan Started at 2305 on 25 April 1984 During the Incineration of the Violet IV Smoke. Ex = 226 nm, Em = 306 nm.

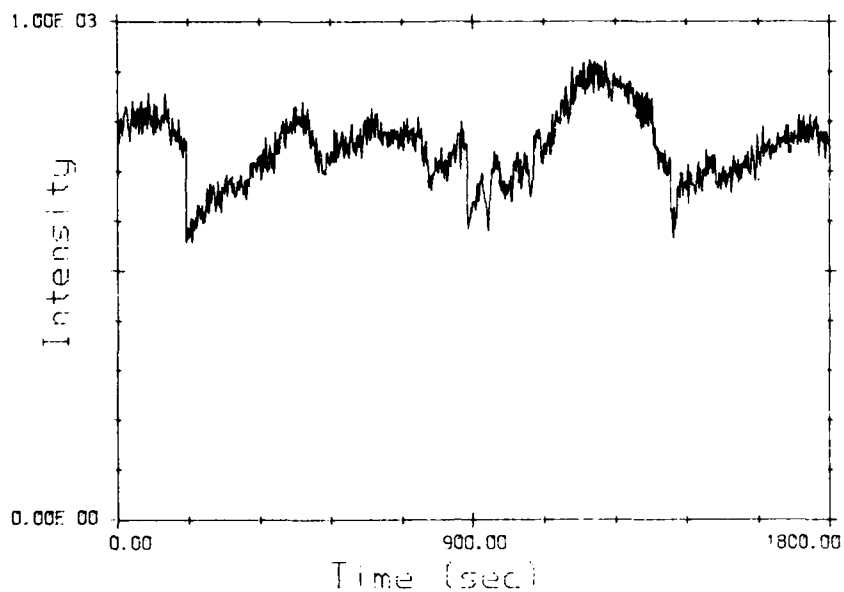


FIGURE 23. Temporal Scan Started at 2332 on 25 April 1984 During the Switch from the Violet IV to the Red III Smoke. The switch was made 800 seconds into the scan. Ex = 226 nm, Em = 306 nm.

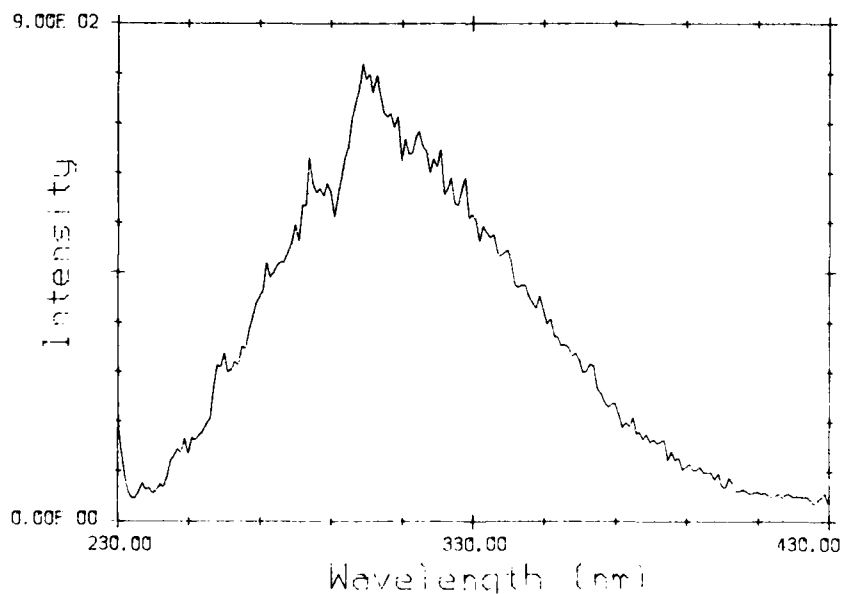


FIGURE 24. Fluorescence Emission Scan Started at 0007 on 26 April 1984 During the Incineration of the Red III Smoke. Ex = 226 nm.

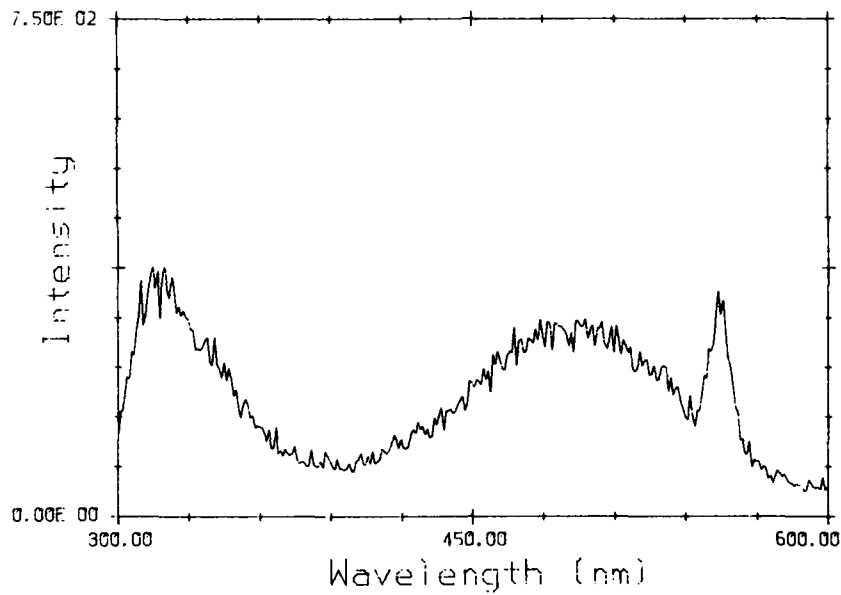


FIGURE 25. Fluorescence Emission Scan Started at 0018 on 26 April 1984 During the Incineration of the Red III Smoke. Ex = 277 nm.

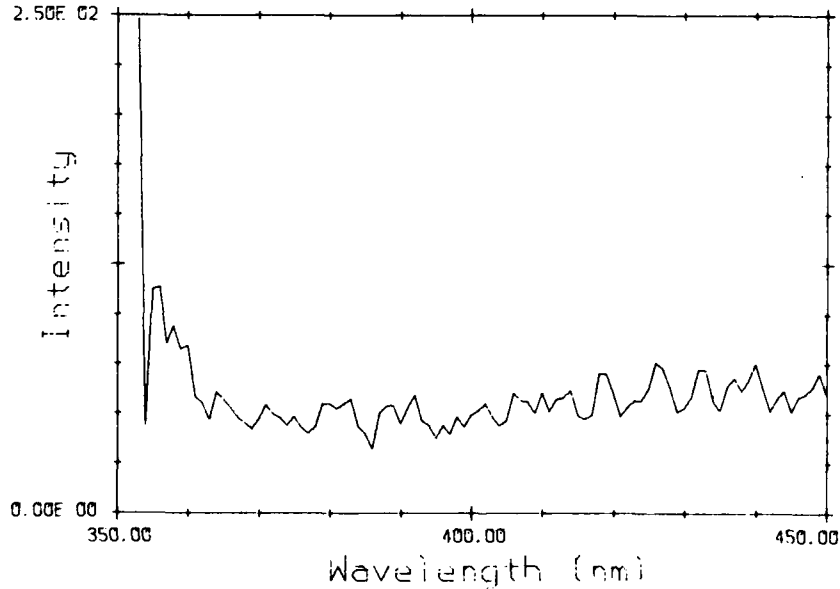


FIGURE 26. Fluorescence Emission Scan Started at 0027 on 26 April 1984 During the Incineration of the Red III Smoke. Ex = 344 nm. Excitation parameter for anthracene detection.

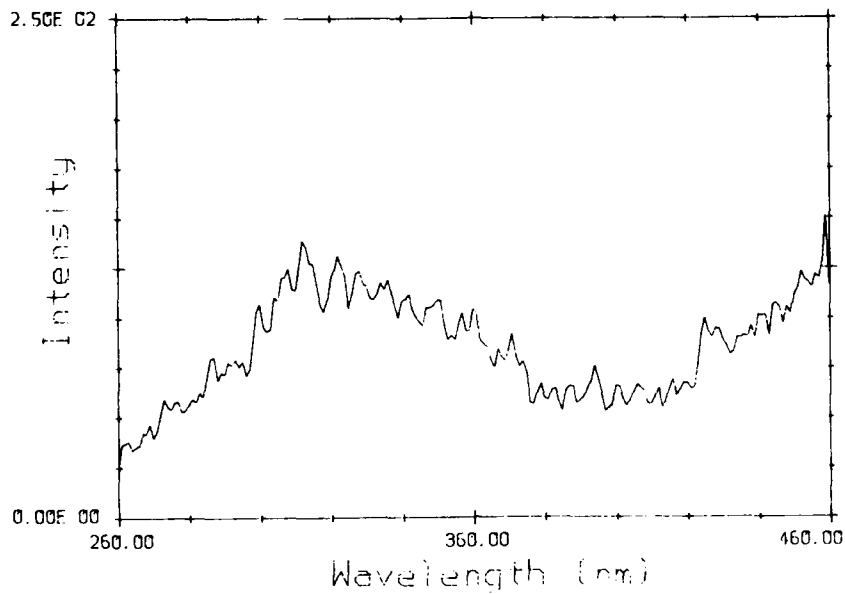


FIGURE 27. Fluorescence Emission Scan Started at 0032 on 26 April 1984 During the Incineration of the Red III Smoke. Ex = 240 nm.

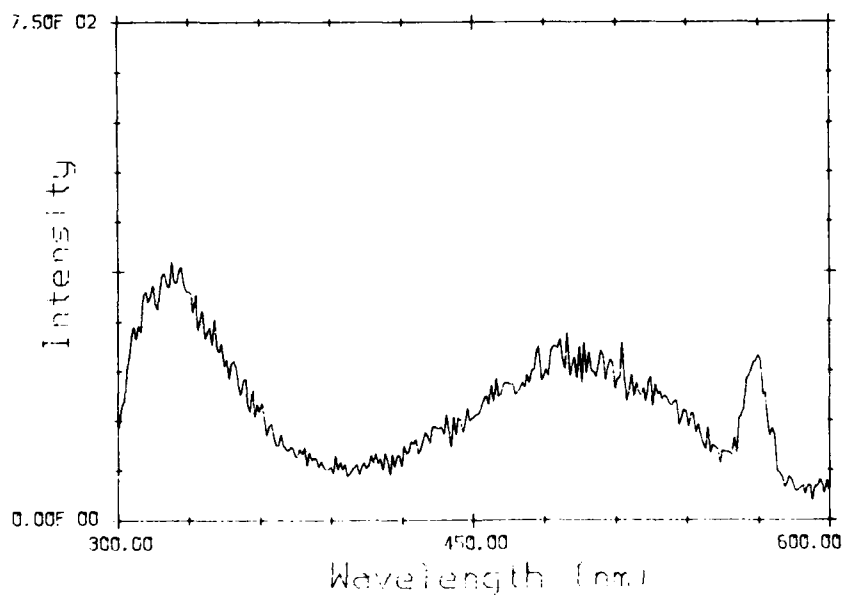


FIGURE 28. Fluorescence Emission Scan Started at 0040 on 26 April 1984 During the Incineration of the Red III Smoke. Ex = 284 nm. Excitation parameter for phenanthrene detection.

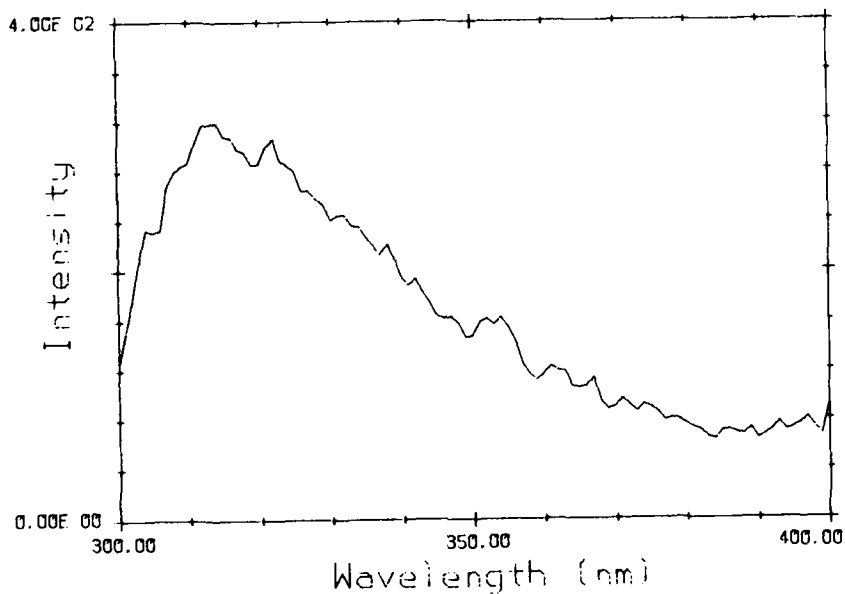


FIGURE 29. Fluorescence Emission Scan Started at 0050 on 26 April 1984 During the Incineration of the Red III Smoke. Ex = 269 nm. Excitation parameter for naphthalene detection.

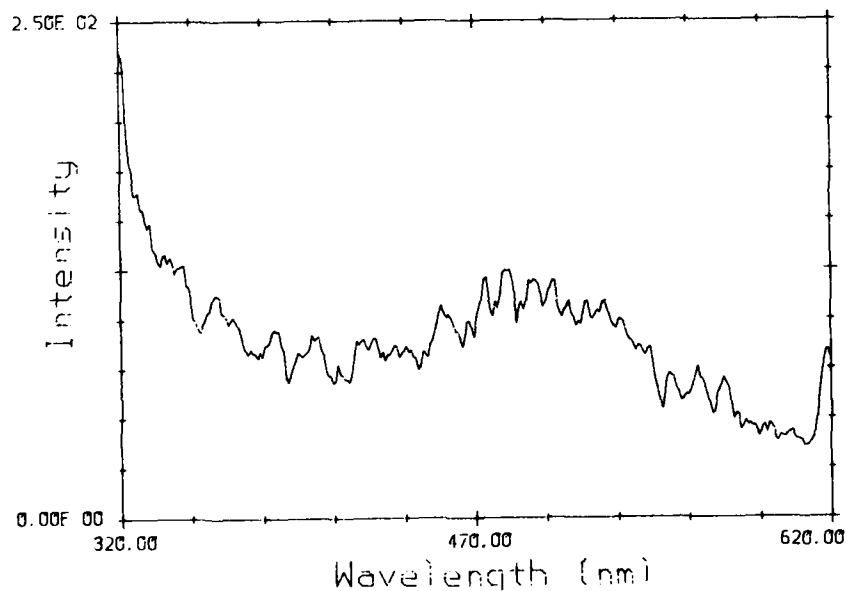


FIGURE 30. Fluorescence Emission Scan Started at 0055 on 26 April 1984 During the Incineration of the Red III Smoke. Ex = 310 nm.

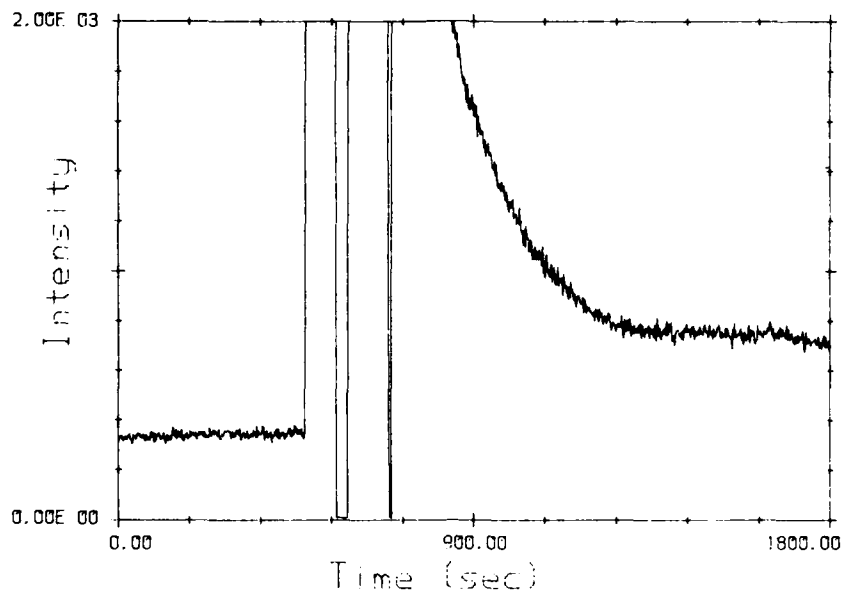


FIGURE 31. Temporal Scan Started at 0104 on 26 April 1984 During the Incineration of the Red III Smoke. The dramatic increase in signal near 460 seconds was caused by liquid water from the sampling location spraying through the flow cell. Ex = 277 nm, Em = 318 nm.

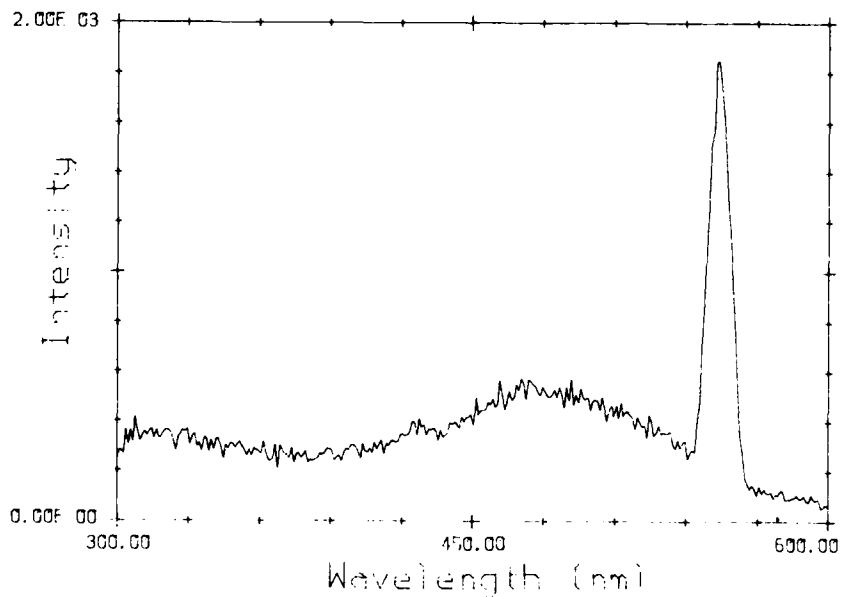


FIGURE 32. Fluorescence Emission Scan Started at 0705 on 26 April 1984 During the Incineration of the Red III Smoke. Ex = 277 nm.

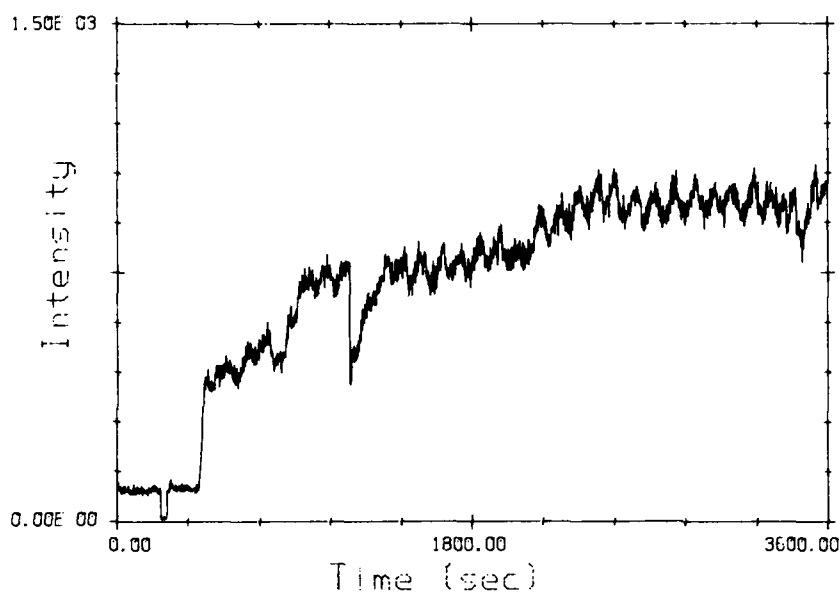


FIGURE 33. Temporal Scan Started at 0924 on 26 April 1984 During the Incineration of the Red III Smoke. Ex = 226 nm, Em = 306 nm.

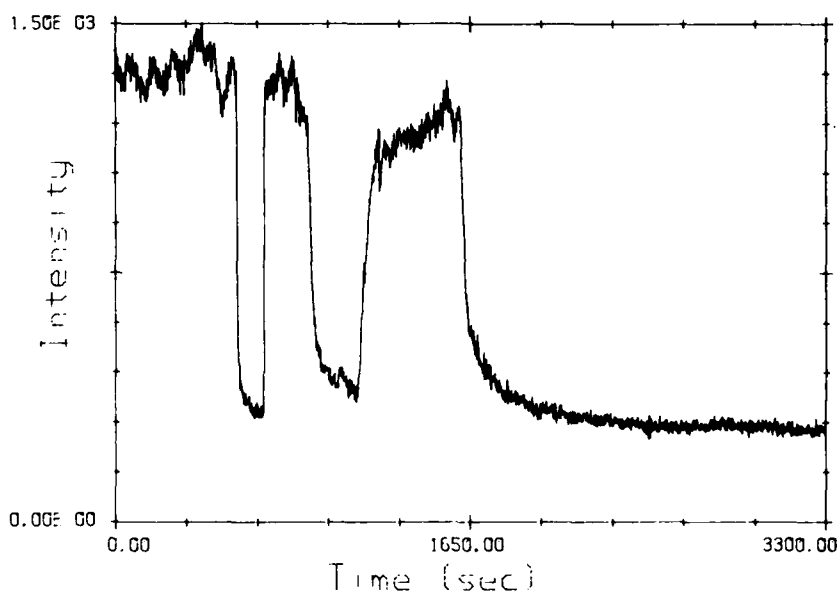


FIGURE 34. Temporal Scan Started at 1205 on 26 April 1984 During the Incineration of the Red III Smoke. Ex = 226 nm, Em = 306 nm. Valves switched to sample room air at 570 seconds and back on-line at 700 seconds. Red III feed turned off at 900 seconds, and back on at 1150 seconds. Feed off again at 1650 seconds.

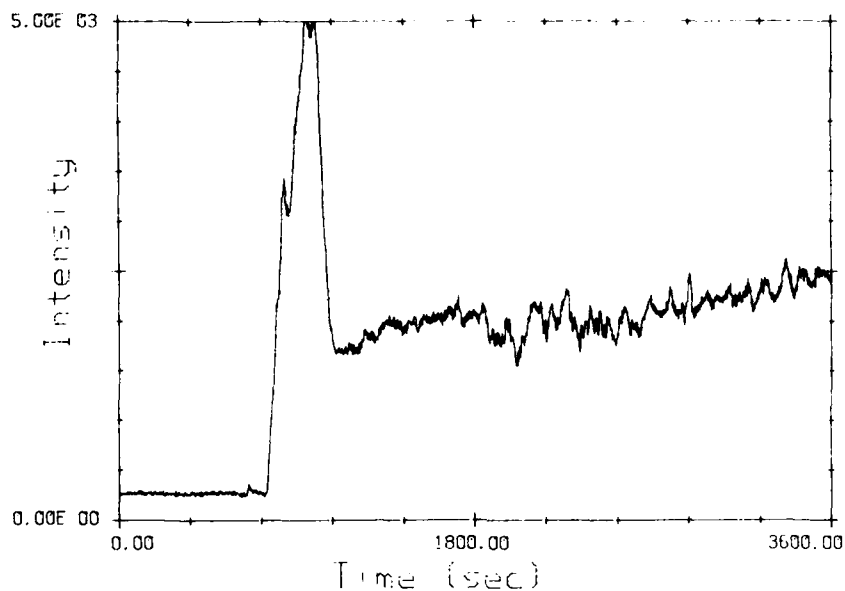


FIGURE 35. Temporal Scan Started at 1303 on 26 April 1984 During the Start of the Incineration of the Green IV Smoke. Ex = 226 nm, Em = 306 nm. The liquid feed was initiated 600 seconds into the scan.

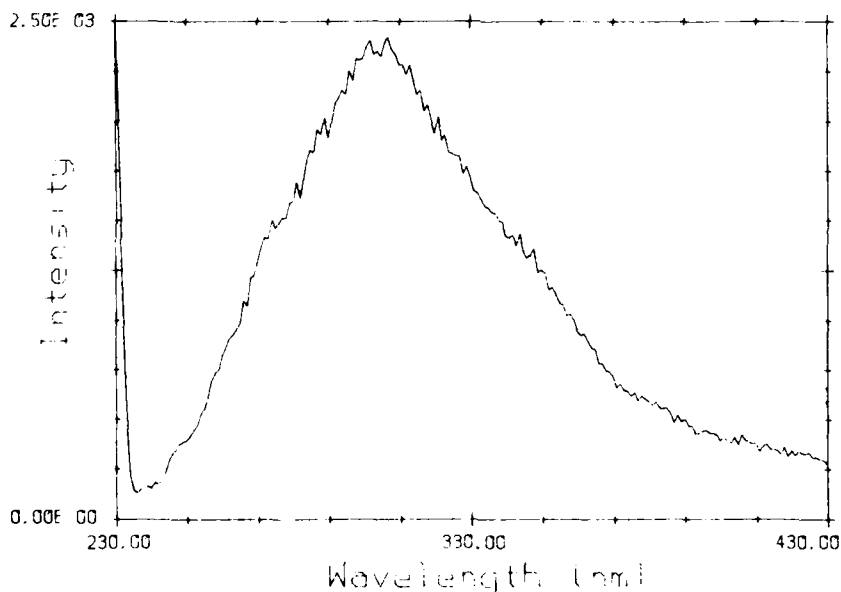


FIGURE 36. Fluorescence Emission Scan Started at 1416 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 226 nm.

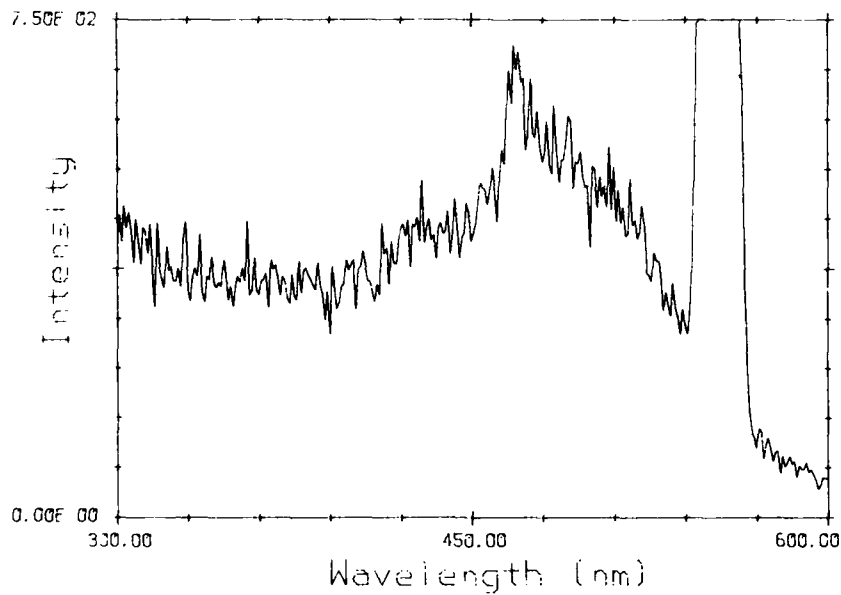


FIGURE 37. Fluorescence Emission Scan Started at 1428 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 277 nm.

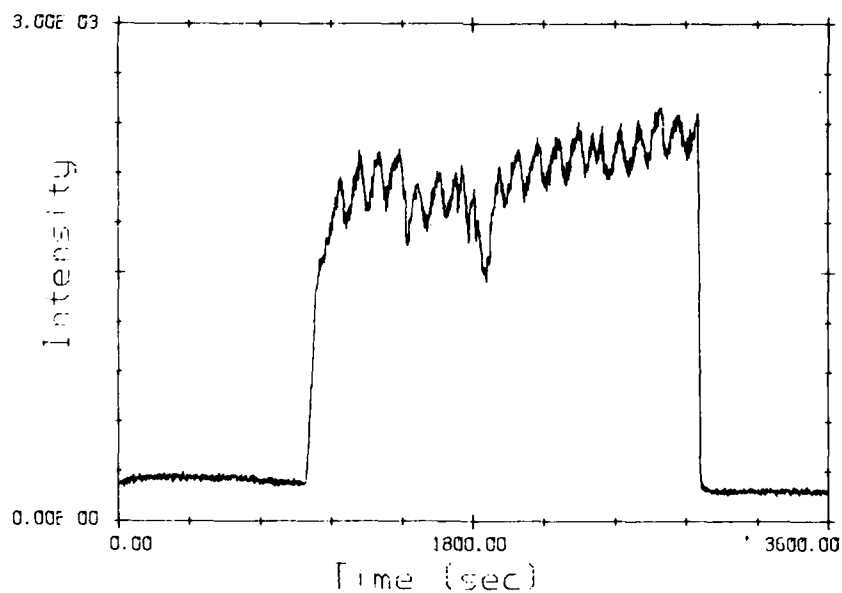


FIGURE 38. Temporal Scan Started at 1435 on 26 April 1984 During the Start of the Incineration of the Green IV Smoke. Ex = 226 nm, Em = 306 nm. The liquid feed was re-started 952 seconds into the scan. Valves switched to sample room air at 3000 seconds.

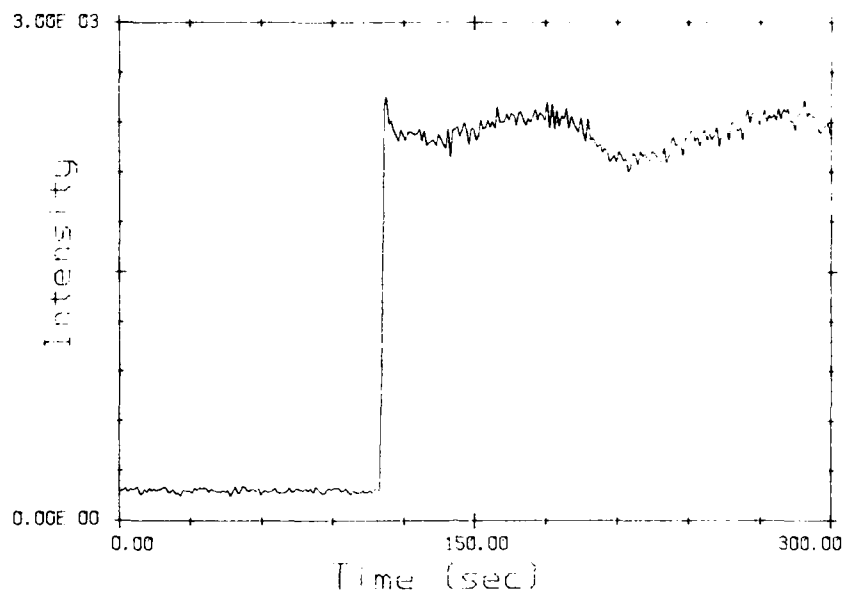


FIGURE 39. Temporal Scan Started at 1539 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 226 nm, Em = 306 nm. Valves switched from sampling room air to on-line at 100 seconds.

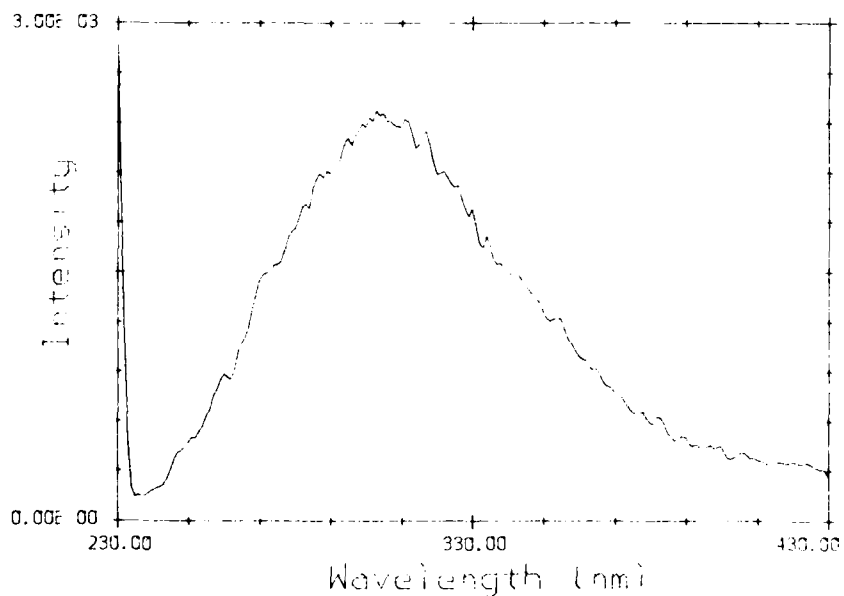


FIGURE 40. Fluorescence Emission Scan Started at 1547 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 226 nm.

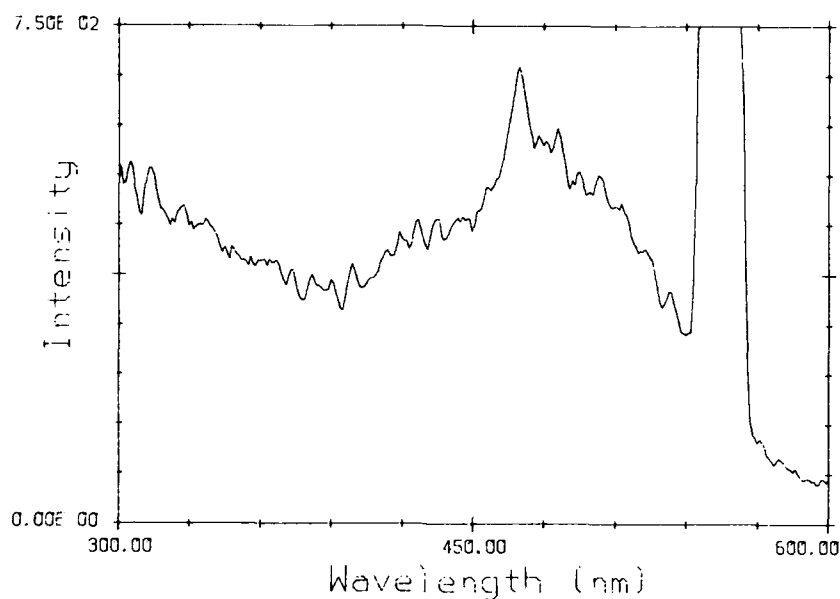


FIGURE 41. Fluorescence Emission Scan Started at 1550 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 277 nm.

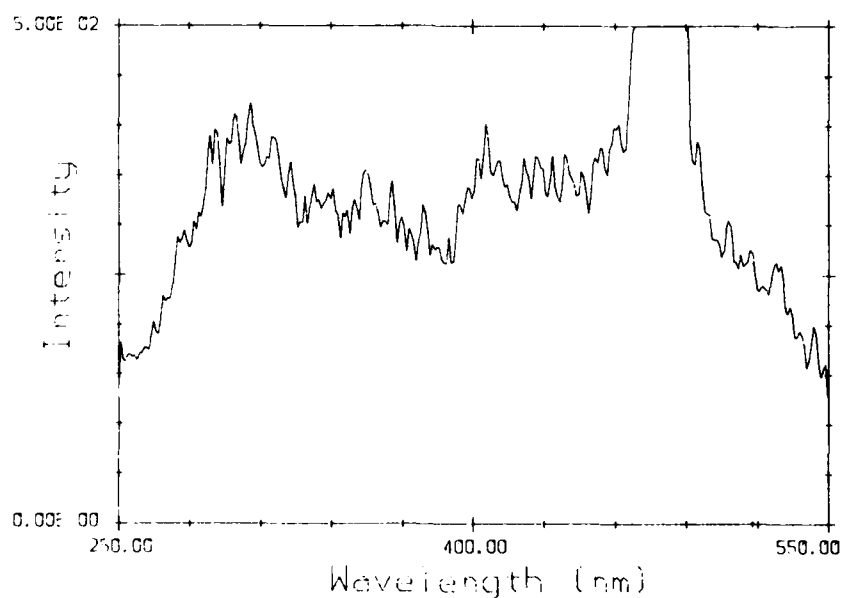


FIGURE 42. Fluorescence Emission Scan Started at 1600 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 240 nm.

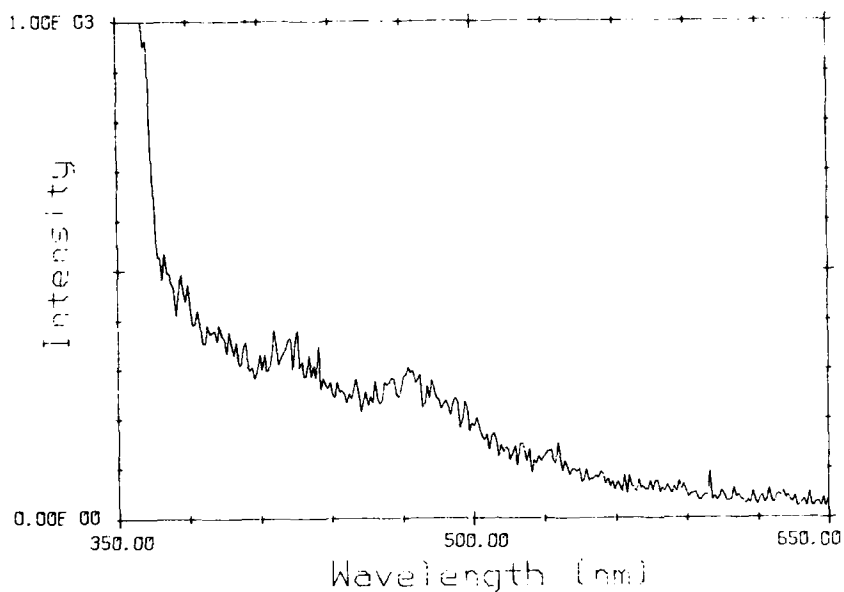


FIGURE 43. Fluorescence Emission Scan Started at 1608 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 344 nm. Excitation parameter for anthracene detection.

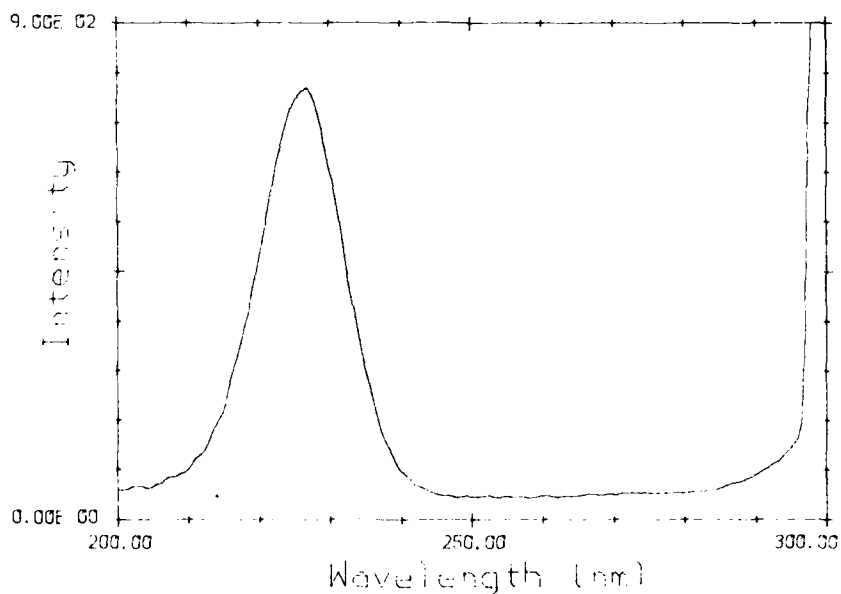


FIGURE 44. Fluorescence Excitation Scan Started at 1632 on 26 April 1984 During the Incineration of the Green IV Smoke. Em = 306 nm, S1/S2 mode.

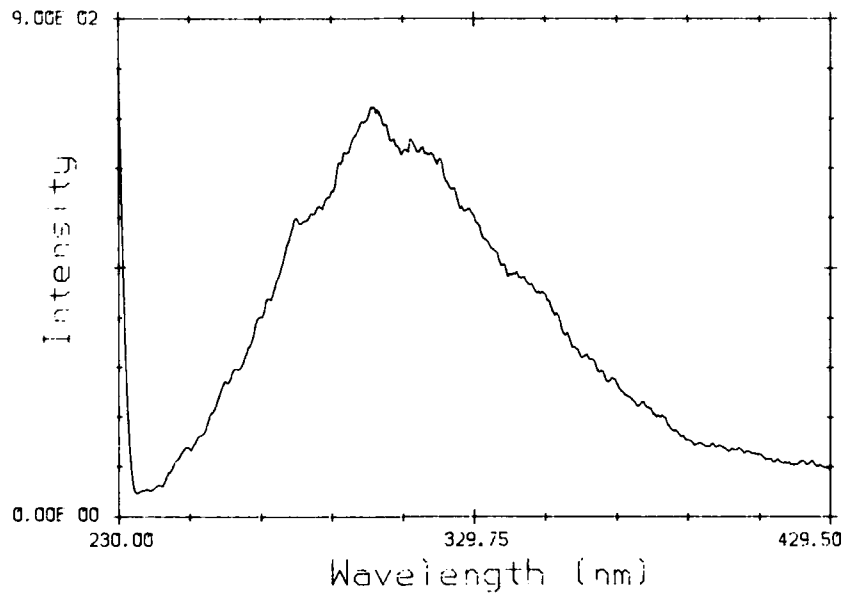


FIGURE 45. Fluorescence Emission Scan Started at 1643 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 226 nm. S1/S2 mode.

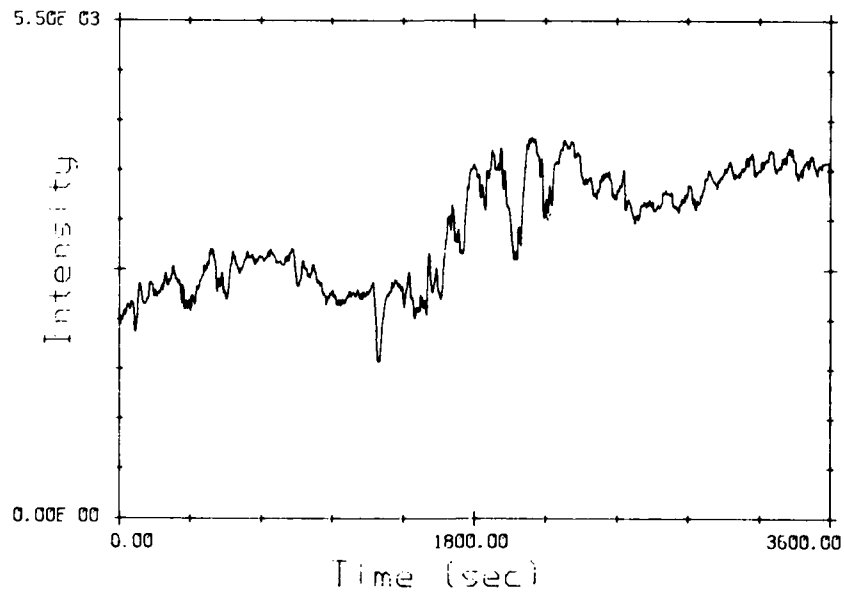


FIGURE 46. Temporal Scan Started at 1705 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 226 nm, Em = 302 nm.

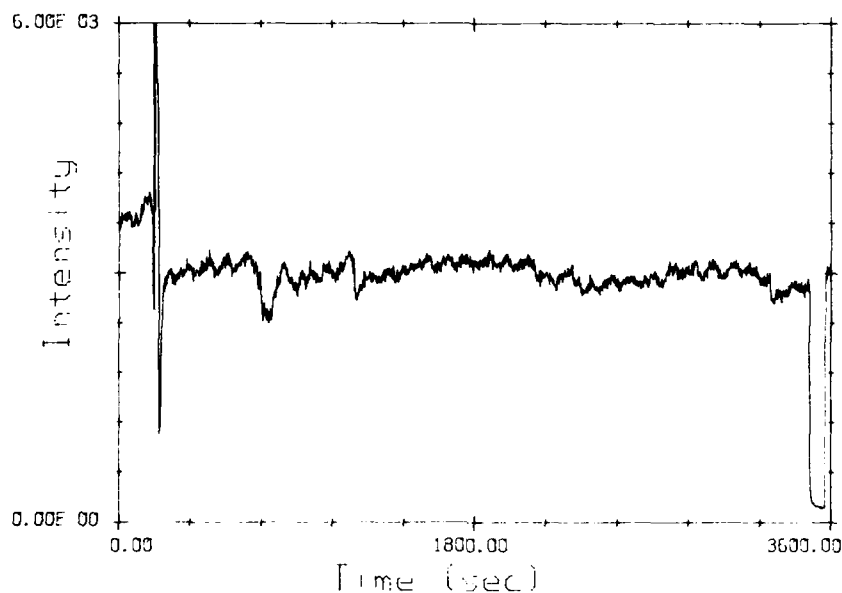


FIGURE 47. Temporal Scan Started at 1821 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 226 nm. Em = 302 nm. The spikes at 202 seconds were caused by pressure fluctuations in the line during the removal of water from the pump trap. Valves switched to sample room air at 3494 seconds, and back on-line at 3570 seconds.

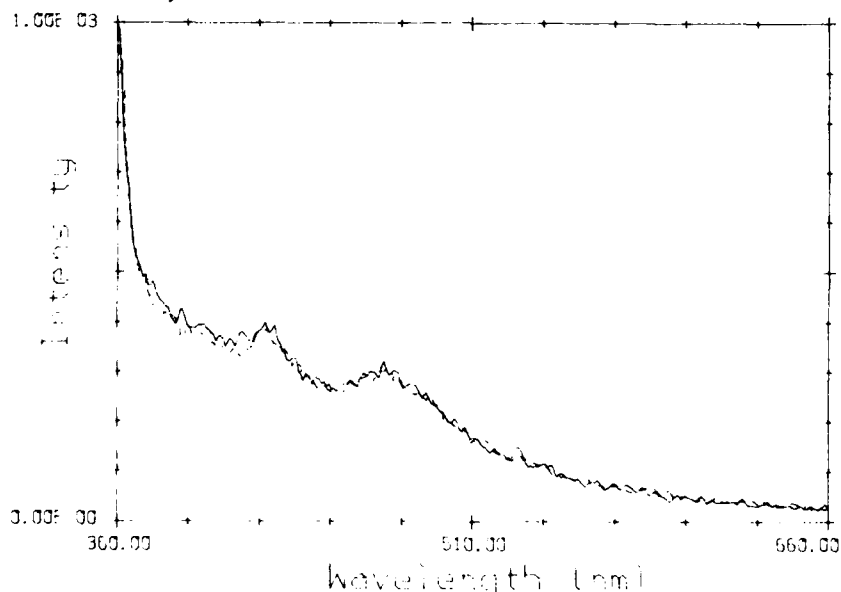


FIGURE 48. Fluorescence Emission Spectrum Started at 1930 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 344 nm, on-line (—), room air (---). Excitation parameter for anthracene detection.

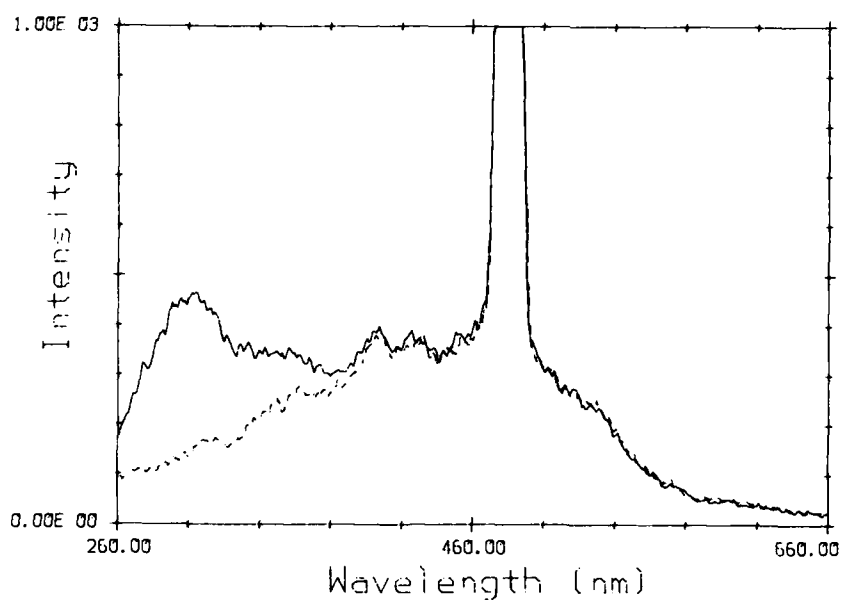


FIGURE 49. Fluorescence Emission Spectrum Started at 1930 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 240 nm, on-line (—), room air (---).

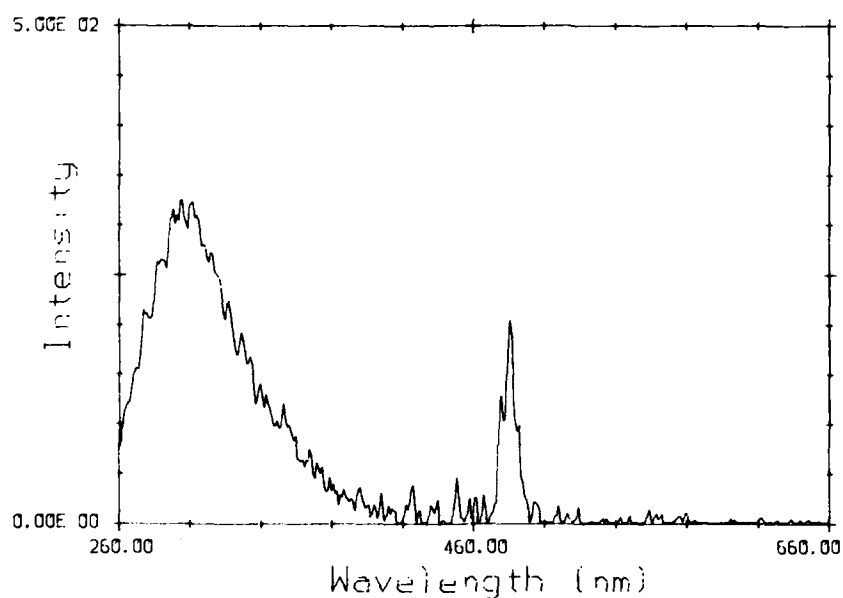


FIGURE 50. Difference Spectrum Obtained By Subtracting the Two Spectra in Figure 49.

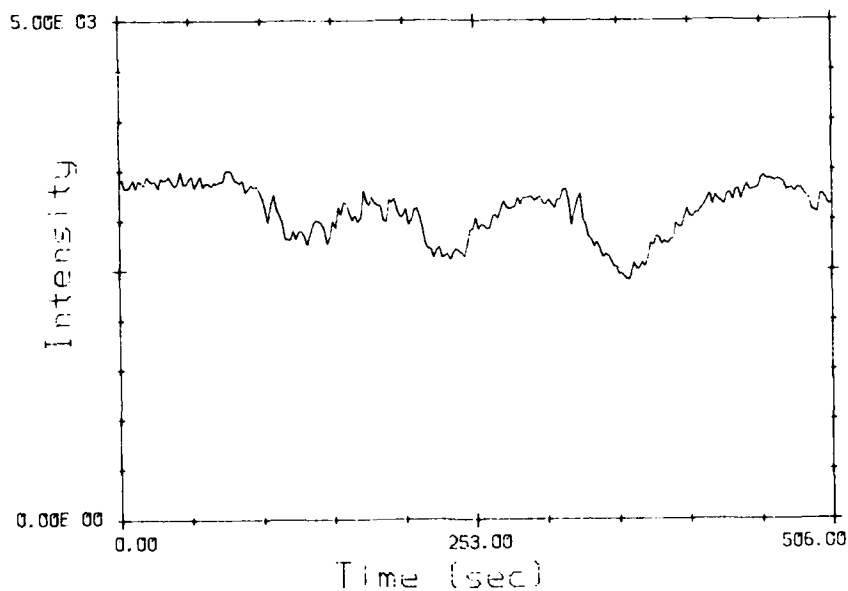


FIGURE 51. Temporal Scan Started at 2052 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 226 nm, Em = 302 nm.

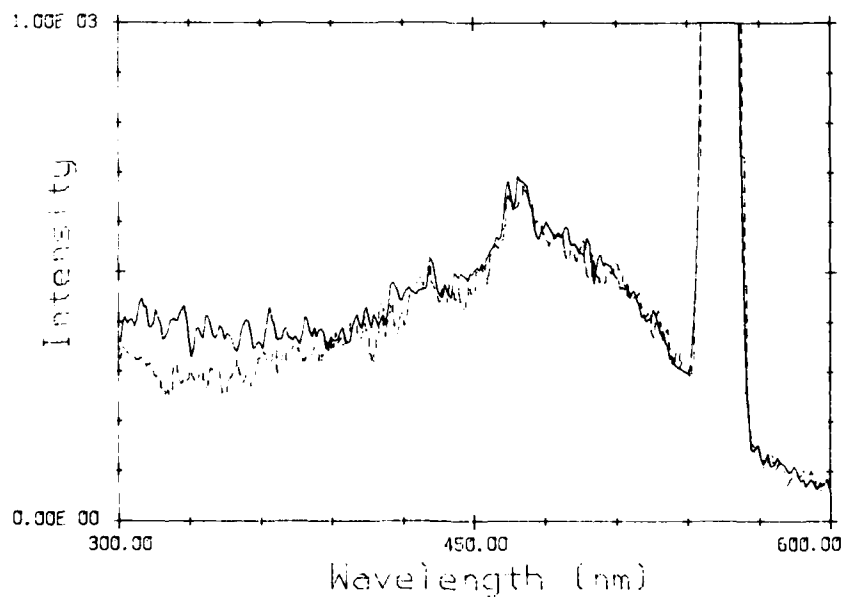


FIGURE 52. Fluorescence Emission Spectrum Started at 2106 on 26 April 1984 During the Incineration of the Green IV Smoke. Ex = 277 nm, on-line (—), room air (---).

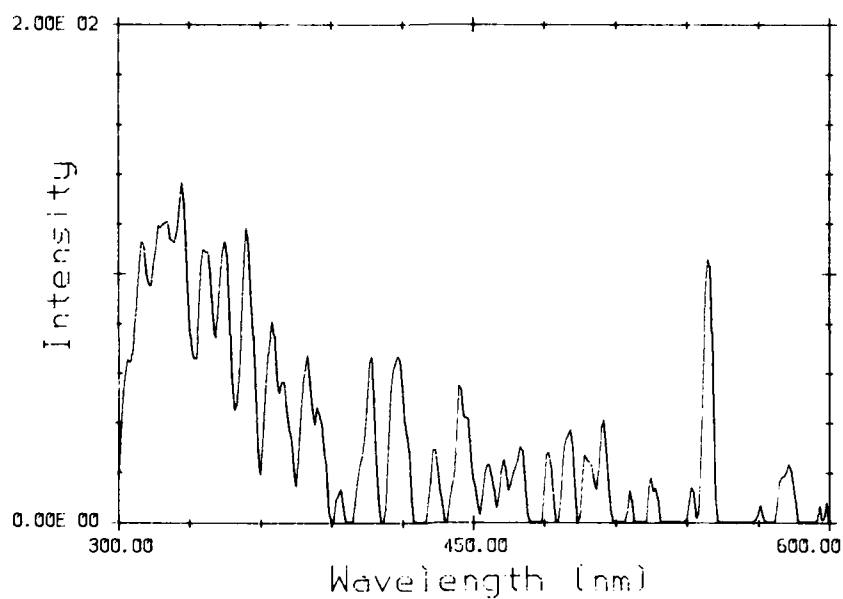


FIGURE 53. Difference Spectrum Obtained by Subtracting the Two Spectra in Figure 52.

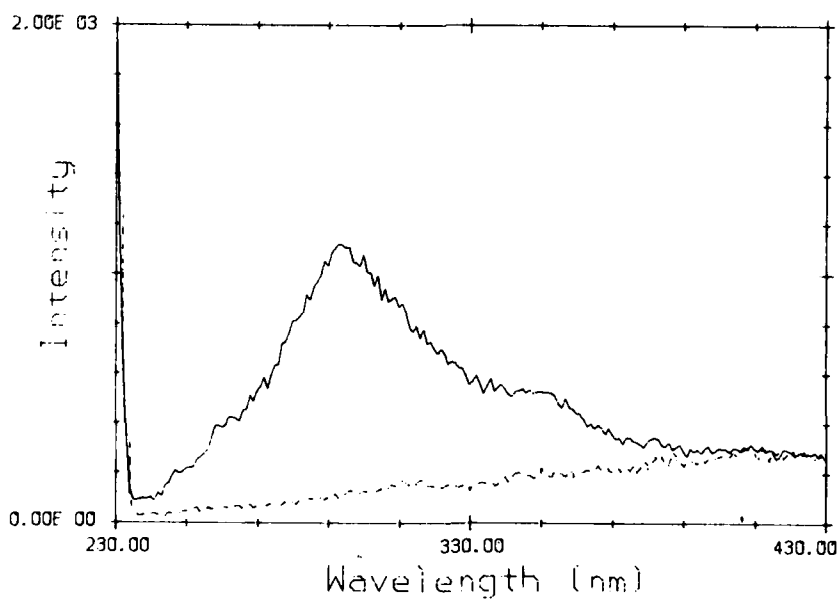


FIGURE 54. Fluorescence Emission Spectrum Started at 2149 on 26 April 1984 During the Incineration of the Yellow VI Smoke. Ex = 226 nm, on-line (—), room air (---).

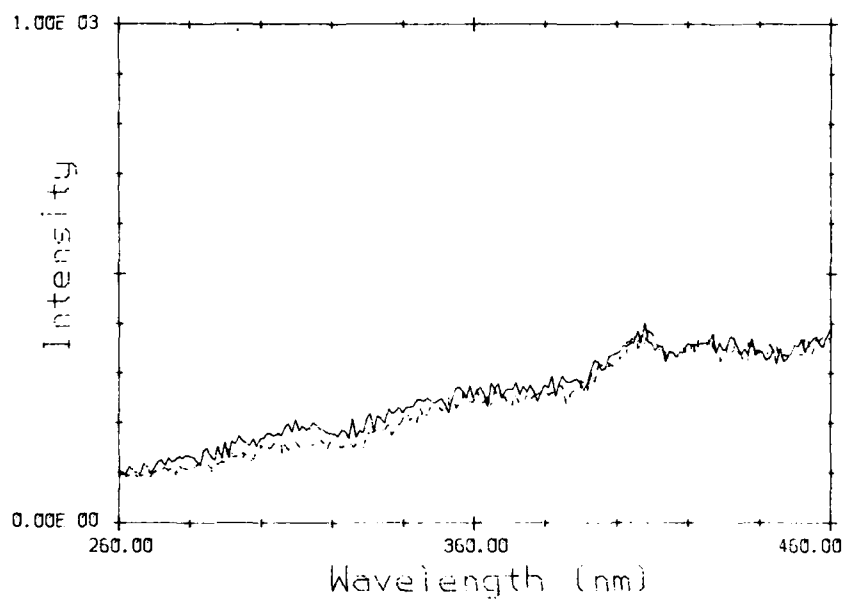


FIGURE 55. Fluorescence Emission Spectrum Started at 2224 on 26 April 1984 During the Incineration of the Yellow VI Smoke. Ex = 240 nm, on-line (—), room air (---).

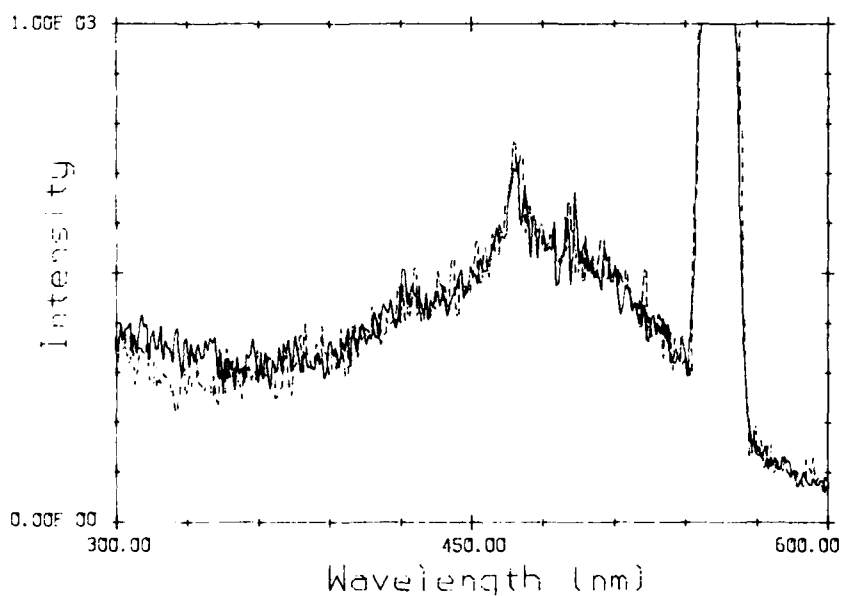


FIGURE 56. Fluorescence Emission Spectrum Started at 225] on 26 April 1984 During the Incineration of the Yellow VI Smoke. Ex = 277 nm, on-line (—), room air (---).

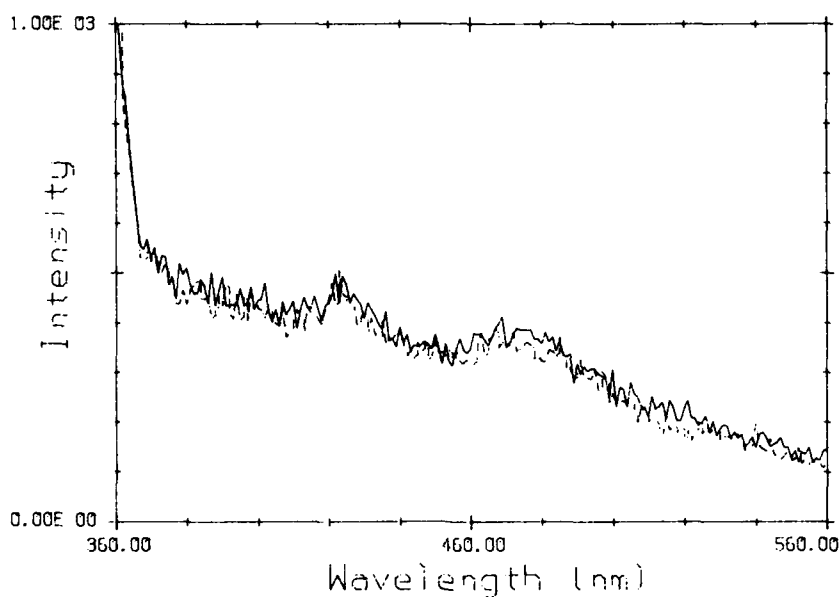


FIGURE 57. Fluorescence Emission Spectrum Started at 23 on 26 April 1984 During the Incineration of the Yellow VI Smoke. Ex = 344 nm, on-line (—), room air (---). Excitation parameter for anthracene detection.

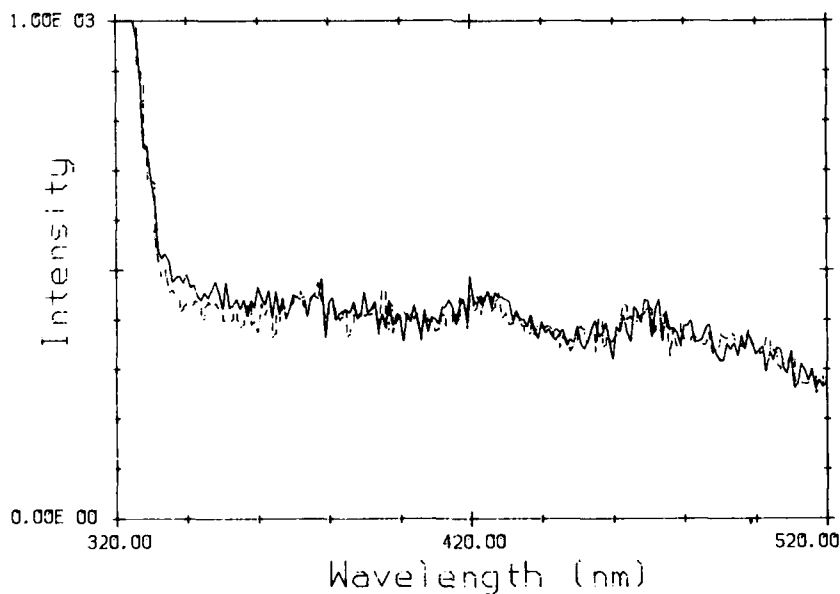


FIGURE 58. Fluorescence Emission Spectrum Started at 2334 on 26 April 1984 During the Incineration of the Yellow VI Smoke. Ex = 310 nm, on-line (—), room air (---).

NWC TP 6559

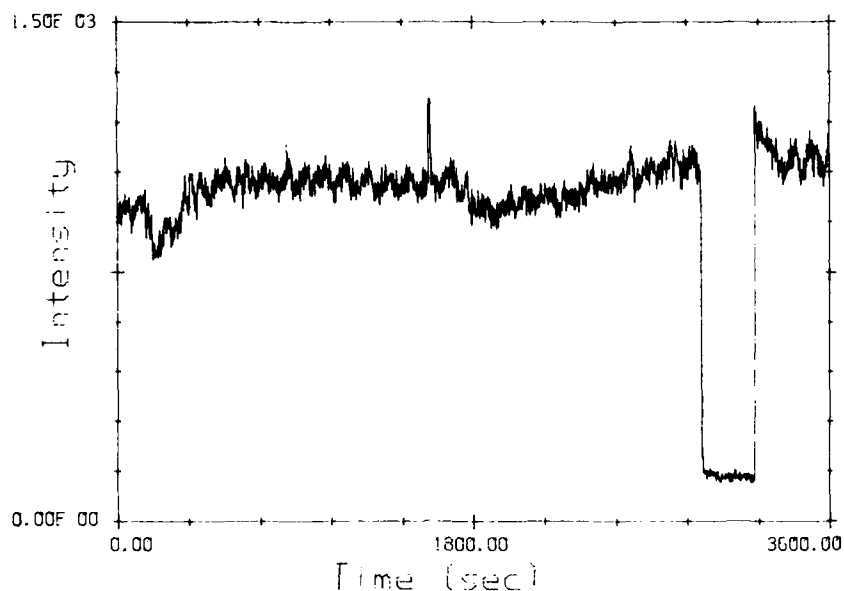


FIGURE 59. Temporal Scan Started at 0125 on 27 April 1984 During the Incineration of the Yellow VI Smoke. Ex = 226 nm, Em = 302 nm. Valves switched to sample room air at 2960 seconds and back on-line at 3224 seconds.

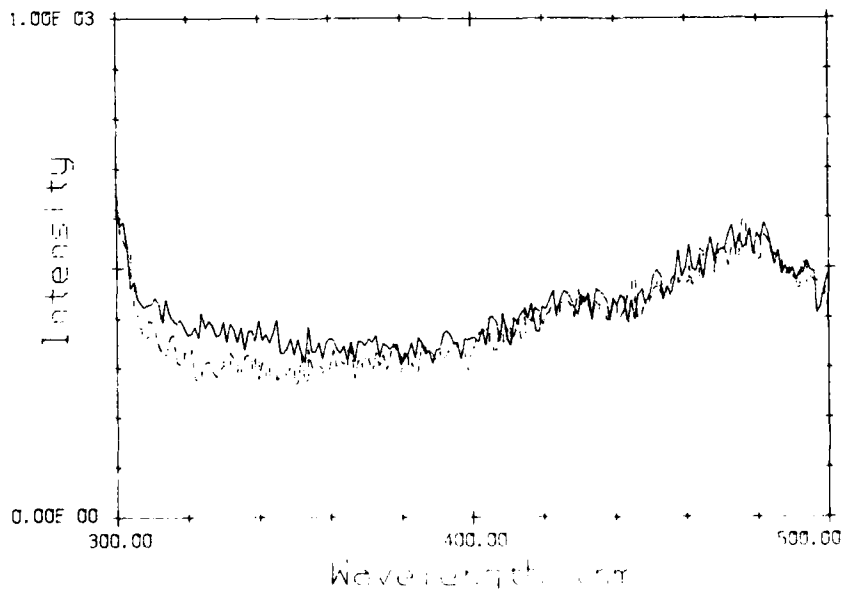


FIGURE 60. Fluorescence Emission Spectrum Started at 0238 on 27 April 1984 During the Incineration of the Yellow VI Smoke. Ex = 284 nm, on-line (—), room air (---). Excitation parameter for phenanthrene detection.

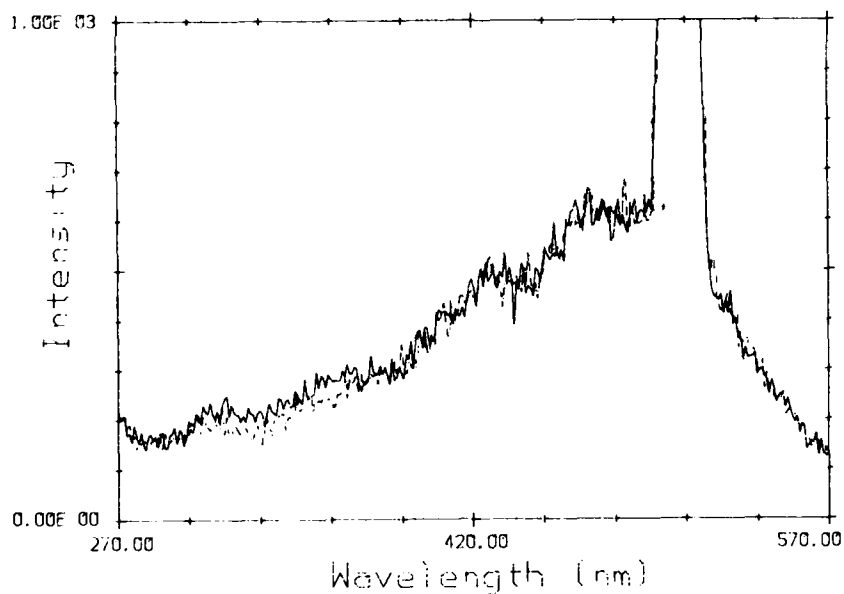


FIGURE 61. Fluorescence Emission Spectrum Started at 0304 on 27 April 1984 During the Incineration of the Yellow VI Smoke. Ex = 254 nm, on-line (—), room air (---). Excitation parameter for benzene detection.

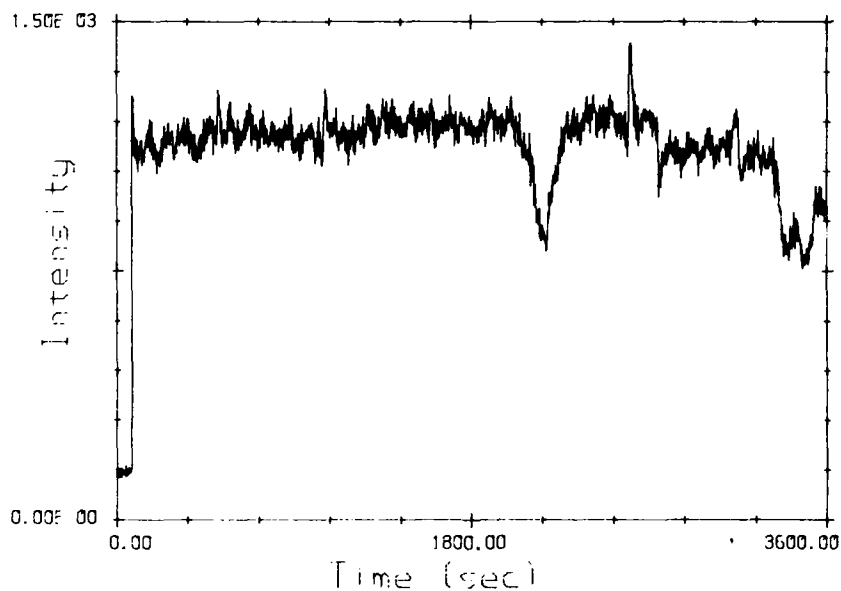


FIGURE 62. Temporal Scan Started at 0328 on 27 April 1984 During the Incineration of the Yellow VI Smoke. Ex = 226 nm, Em = 302 nm. Valves switched from sample room air to on-line at 90 seconds.

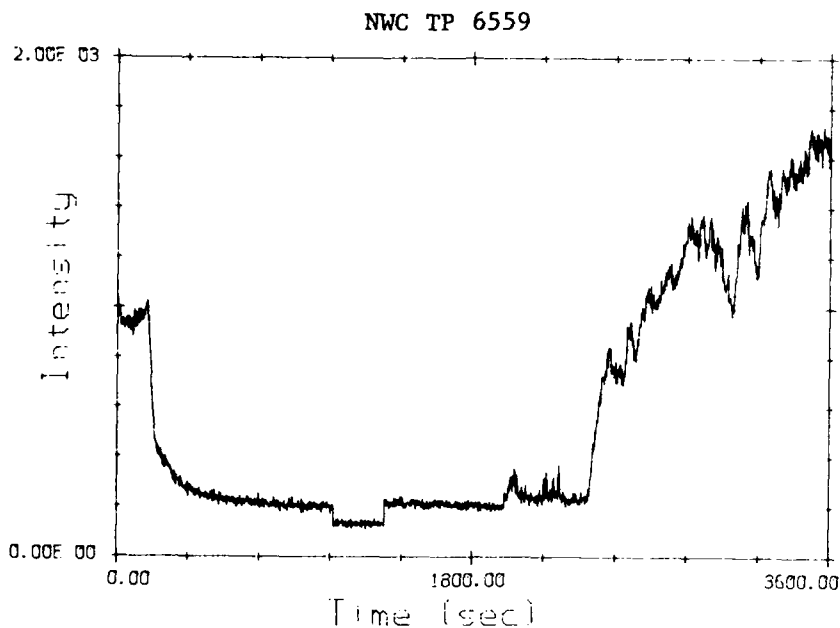


FIGURE 63. Temporal Scan Started at 0431 on 27 April 1984 During the Incineration Changeover from the Yellow VI Smoke to the Green VII Smoke. Ex = 226 nm, Em = 302 nm. The Yellow VI feed was stopped at 100 seconds. Valves switched to sample room air at 1100 seconds, and back on-line at 1360 seconds. The Green VII smoke feed was started at 2450 seconds.

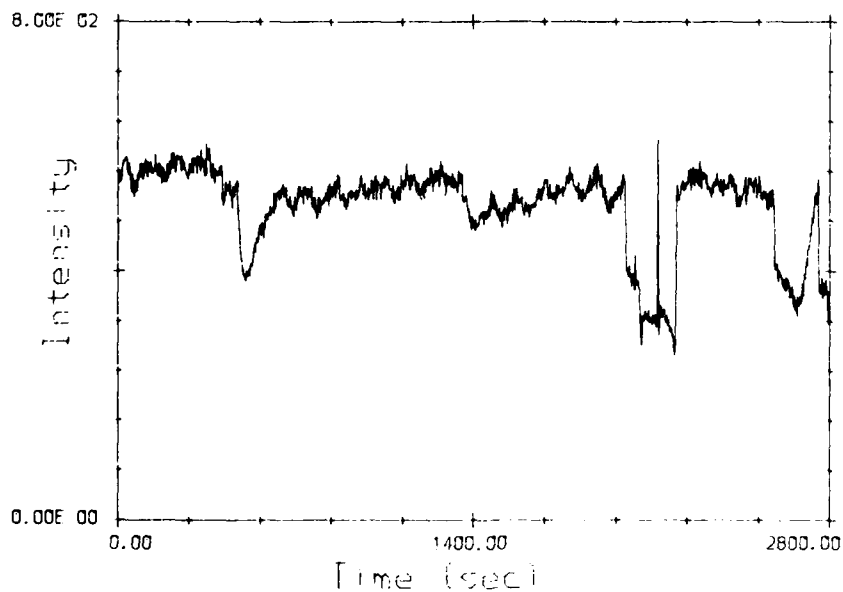


FIGURE 64. Temporal Scan Started at 0534 on 27 April 1984 During the Incineration of the Green VII Smoke. Ex = 226 nm, Em = 302 nm. S1/S2 mode.

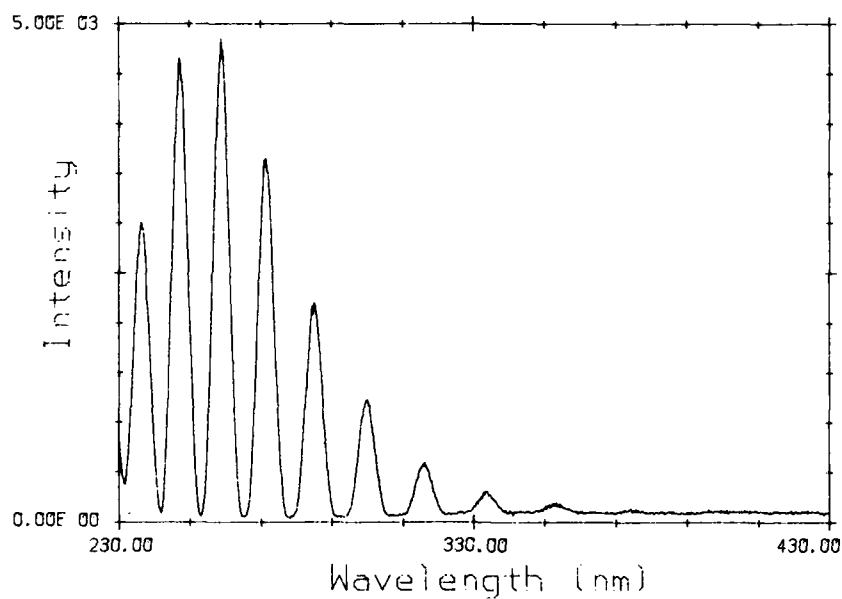


FIGURE 65. Fluorescence Emission Scan Started at 0658 on 27 April 1984. The sample was 244 ppm NO in nitrogen. Ex = 226 nm, S1/S2 mode.

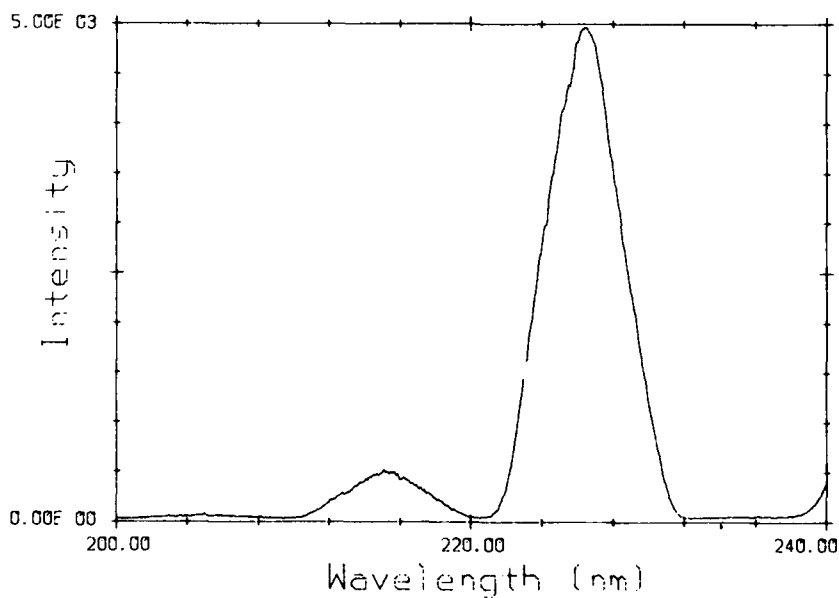


FIGURE 66. Fluorescence Excitation Scan Started at 0714 on 27 April 1984. The sample was 244 ppm NO in nitrogen. Em = 247.2 nm, S1/S2 mode.

NWC TP 6559

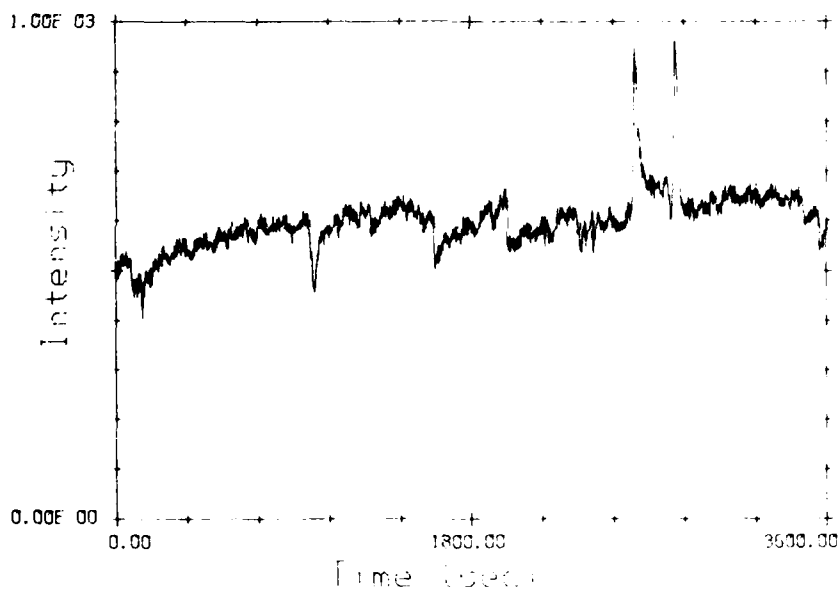


FIGURE 67. Temporal Scan Started at 0822 on 27 April 1984 During the Incineration of the Green VII Smoke. Ex = 226 nm, Em = 302 nm, S1/S2 mode.

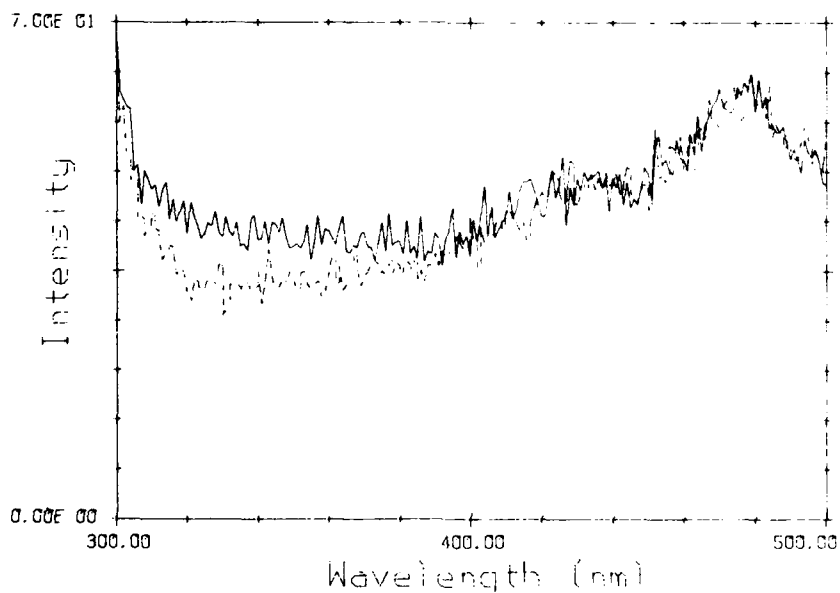


FIGURE 68. Fluorescence Emission Spectrum Started at 0951 on 27 April 1984 During the Incineration of the Green VII smoke. Ex = 284 nm, on-line (—), room air (---). Excitation parameter for phenanthrene detection. S1/S2 mode.

NWC TP 6559

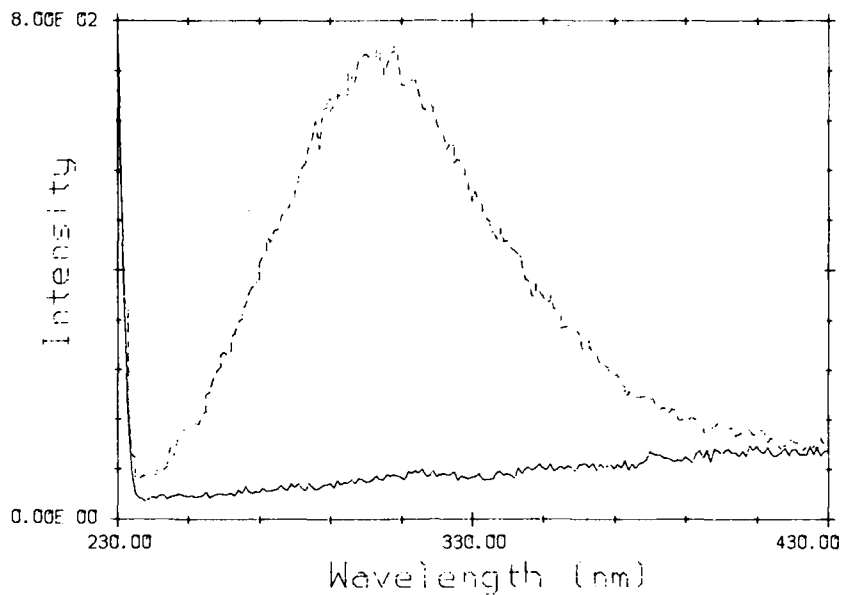


FIGURE 69. Fluorescence Emission Spectrum Started at 1023 on 27 April 1984 During the Incineration of the Green VII Smoke. Ex = 226.5 nm, on-line (---), room air (—). Excitation parameter for NO detection. S1/S2 mode.

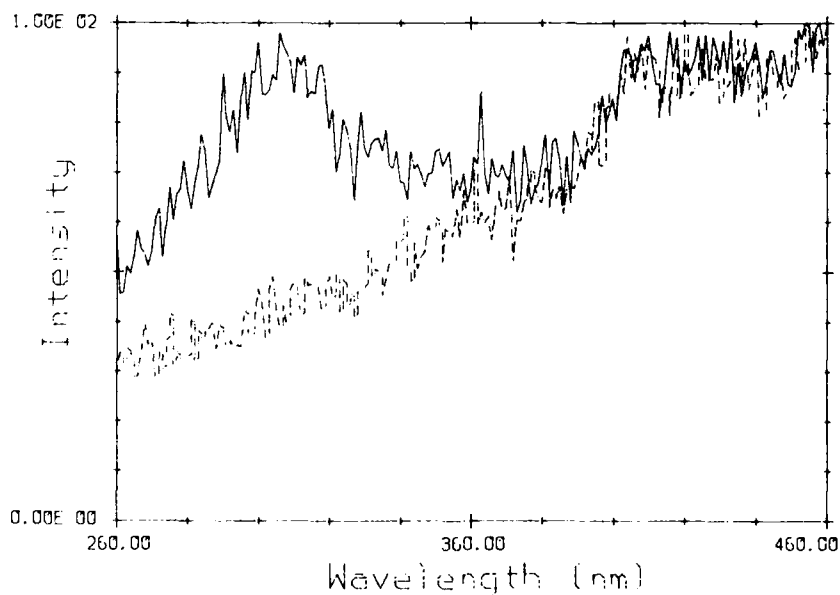


FIGURE 70. Fluorescence Emission Spectrum Started at 1052 on 27 April 1984 During the Incineration of the Green VII Smoke. Ex = 240 nm, on-line (—), room air (---). S1/S2 mode.

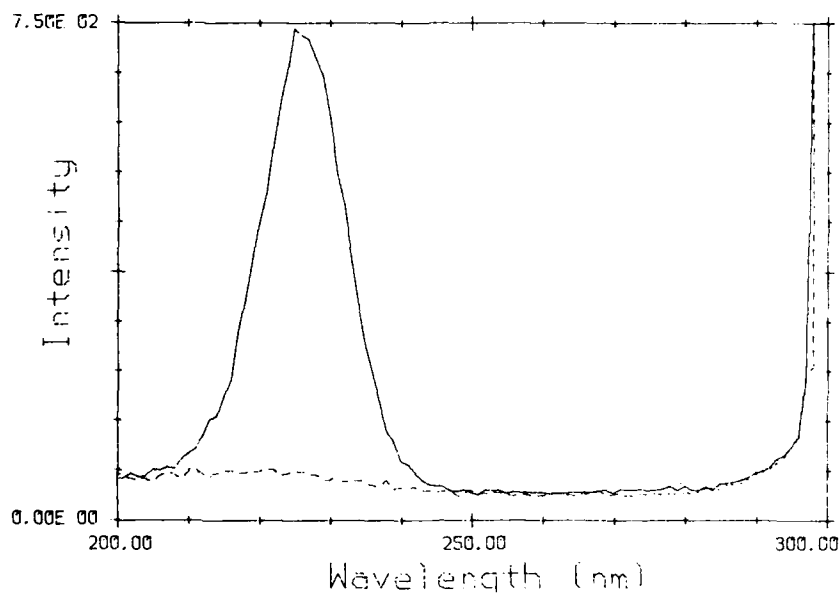


FIGURE 71. Fluorescence Excitation Spectrum Started at 1137 on 27 April 1984 During the Incineration of the Green VII Smoke. $E_m = 306$ nm, on-line (—), room air (---). S1/S2 mode.

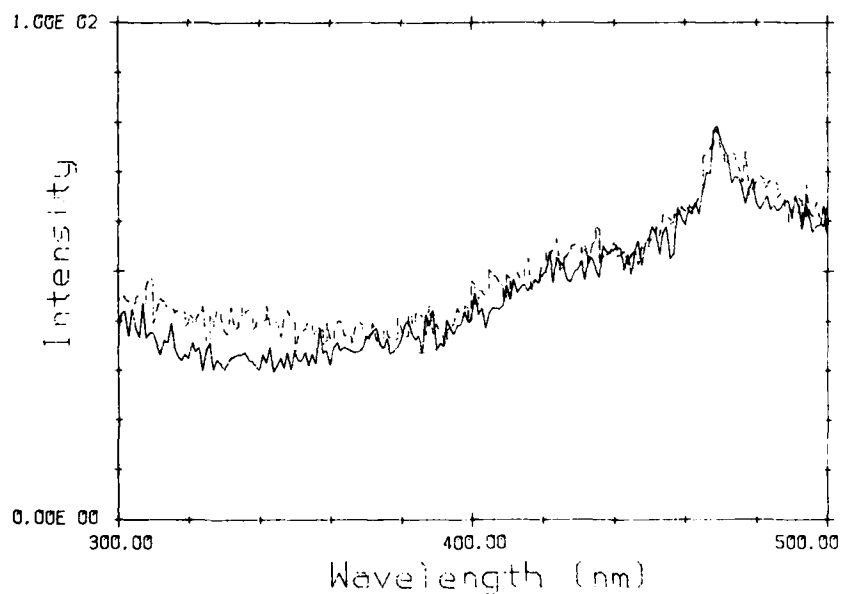


FIGURE 72. Fluorescence Emission Spectrum Started at 1205 on 27 April 1984 During the Incineration of the Green VII Smoke. $E_x = 277$ nm, on-line (---), room air (—). S1/S2 mode.

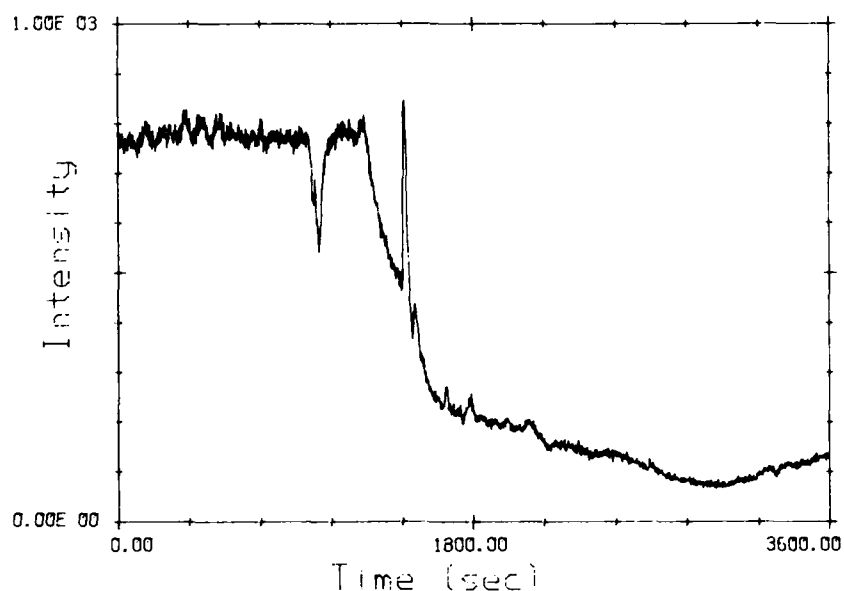


FIGURE 73. Temporal Scan Started at 1220 on 27 April 1984 During the Incineration Change-over from the Green VII Smoke to the Yellow XII Smoke. Ex = 226.5 nm, Em = 302 nm, S1/S2 mode. The switch was made at 1458 seconds.

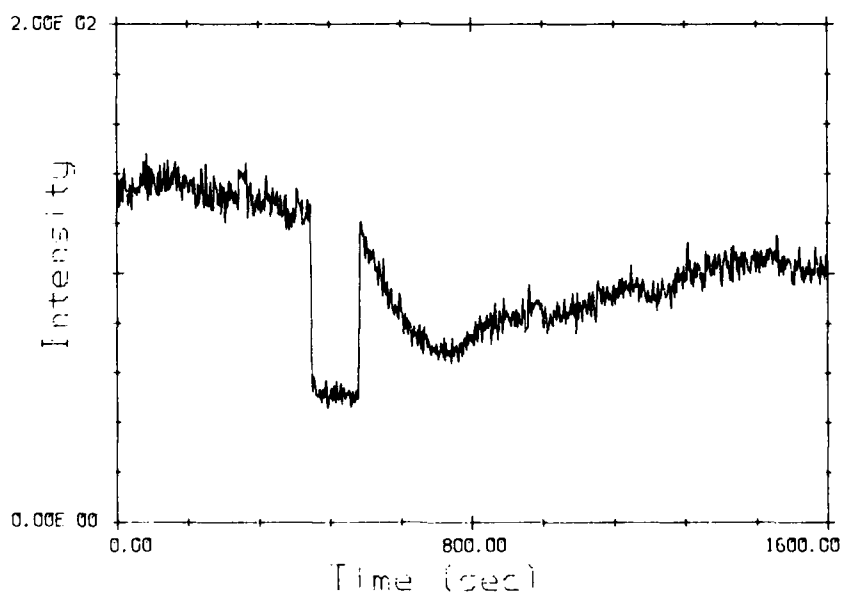


FIGURE 74. Temporal Scan Started at 1324 on 27 April 1984 During the Incineration for the Yellow XII Smoke. Ex = 226.5 nm, Em = 302 nm, S1/S2 mode. Valves switched to monitor room air at 444 seconds, and back on-line at 536 seconds.

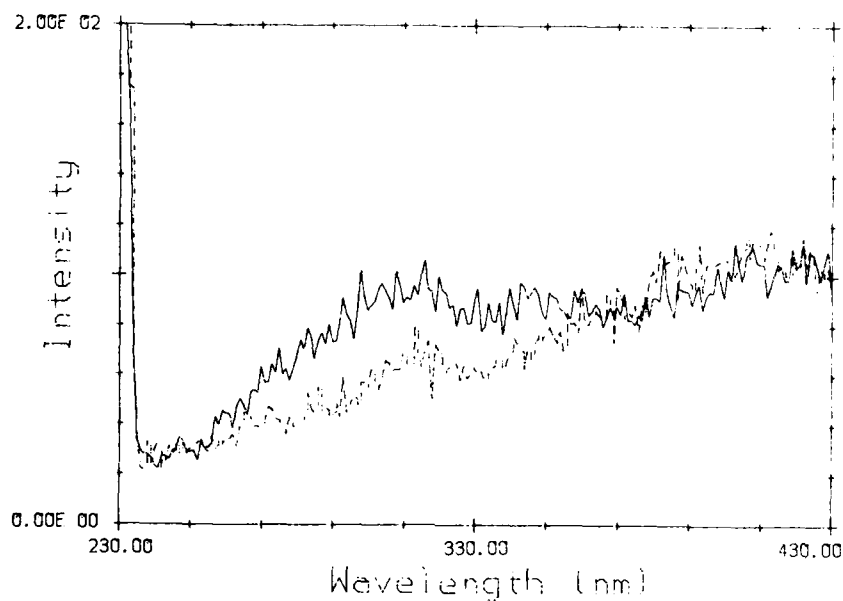


FIGURE 75. Fluorescence Emission Spectrum Started at 1354 on 27 April 1984 During the Incineration of the Yellow XII Smoke. Ex = 226.5 nm, on-line (—), room air (---). Excitation parameter for NO detection. S1/S2 mode.

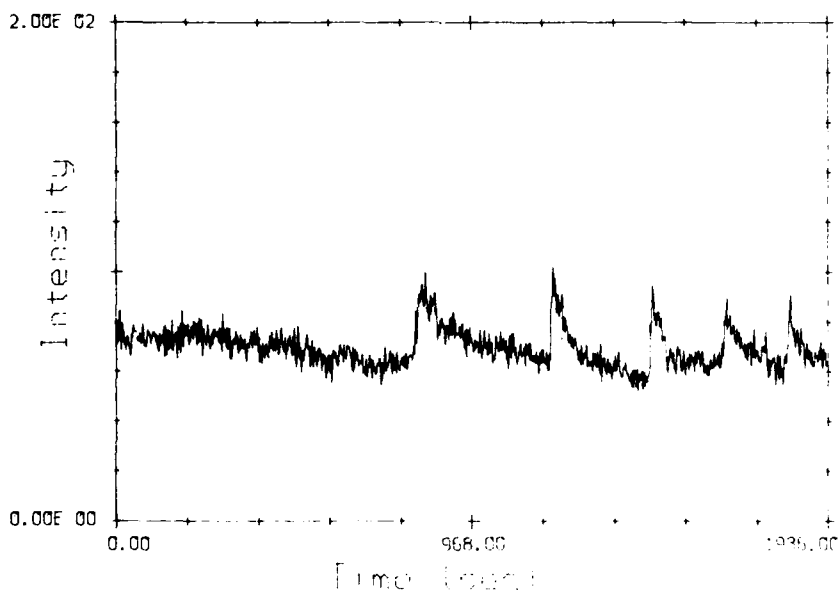


FIGURE 76. Temporal Scan Started at 1416 on 27 April 1984 During the Incineration of the Yellow XII Smoke. Ex = 226.5 nm, Em = 302 nm, S1/S2 mode.

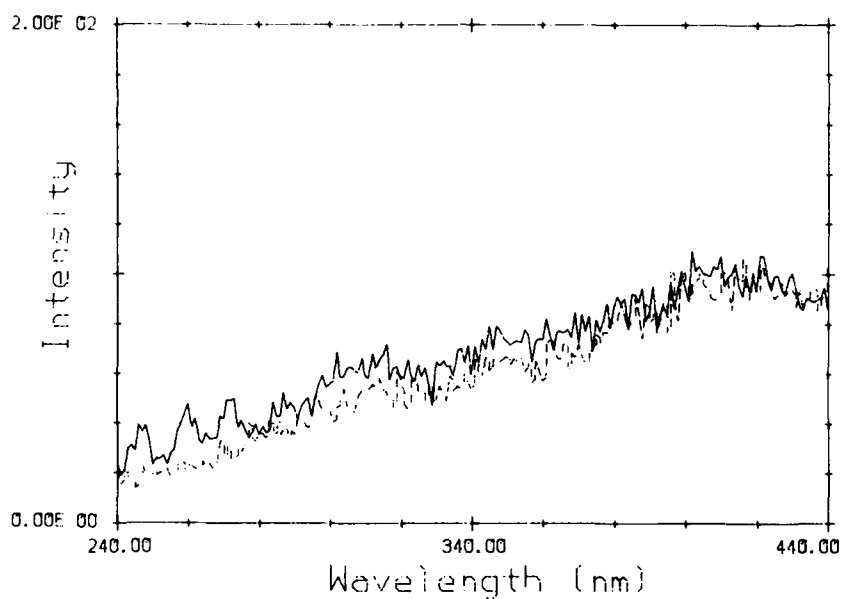


FIGURE 77. Fluorescence Emission Spectrum Started at 1526 on 27 April 1984 During the Incineration of the Yellow XII Smoke. Ex = 226 nm, on-line (—), room air (---). Excitation parameter for NO detection. S1/S2 mode.

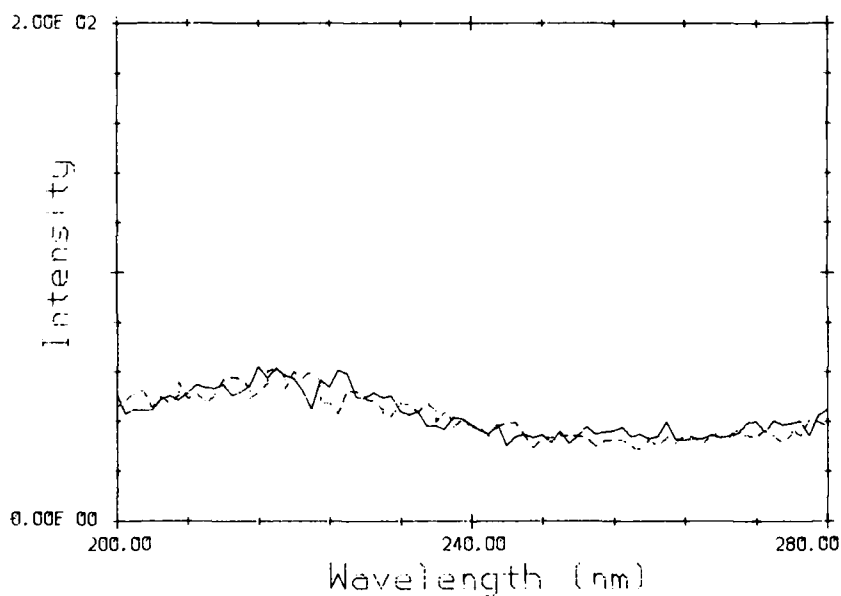


FIGURE 78. Fluorescence Excitation Spectrum Started at 1556 on 27 April 1984 During the Incineration of the Yellow XII Smoke. Ex = 302 nm, on-line (—), room air (---). S1/S2 mode.

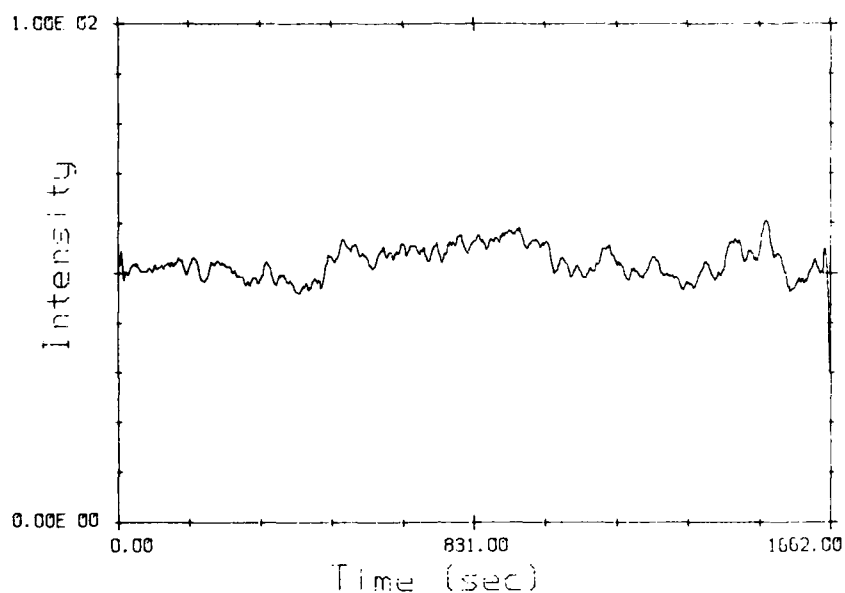


FIGURE 79. Temporal Scan Started at 1615 on 27 April 1984 During the Incineration of the Yellow XII Smoke. Ex = 226 nm, Em = 302 nm. S1/S2 mode. Valves switched off-line to sample room air at 288 seconds, and back on-line at 496 seconds. Repeated at 1018 seconds and 1500 seconds.

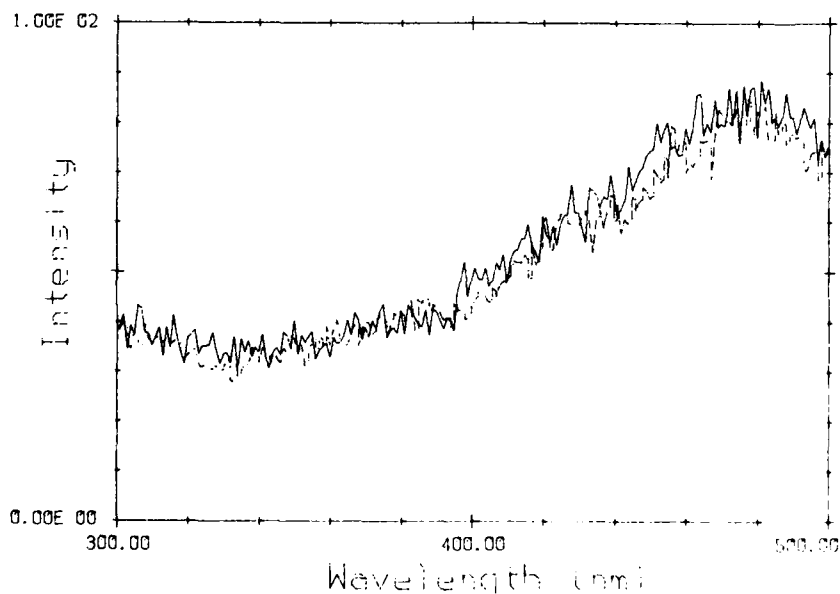


FIGURE 80. Fluorescence Emission Spectrum Started at 1655 on 27 April 1984 During the Incineration of the Yellow XII Smoke. Ex = 269 nm, on-line (—), room air (---). S1/S2 mode. Excitation parameter for naphthalene detection.

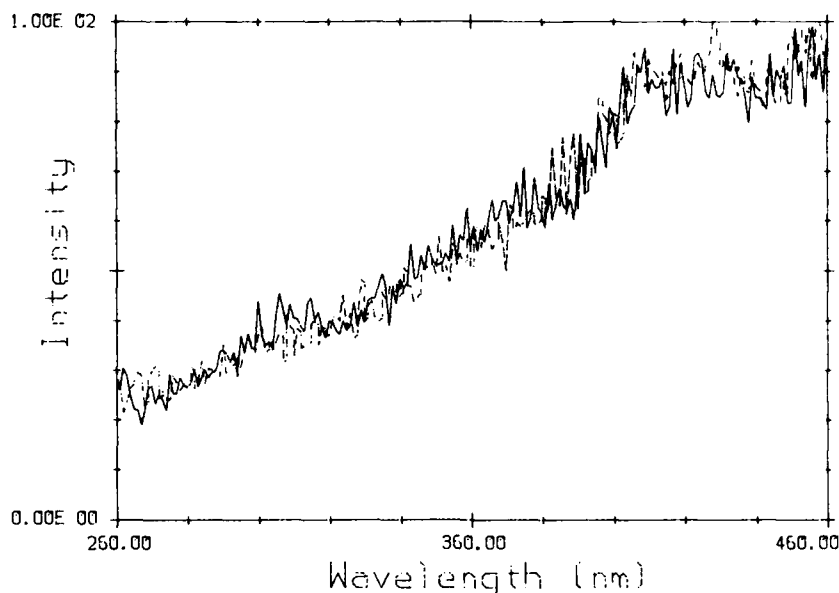


FIGURE 81. Fluorescence Emission Spectrum Started at 1714 on 27 April 1984 During the Incineration of the Yellow XII Smoke. Ex = 240 nm, on-line (—), room air (---). S1/S2 mode.

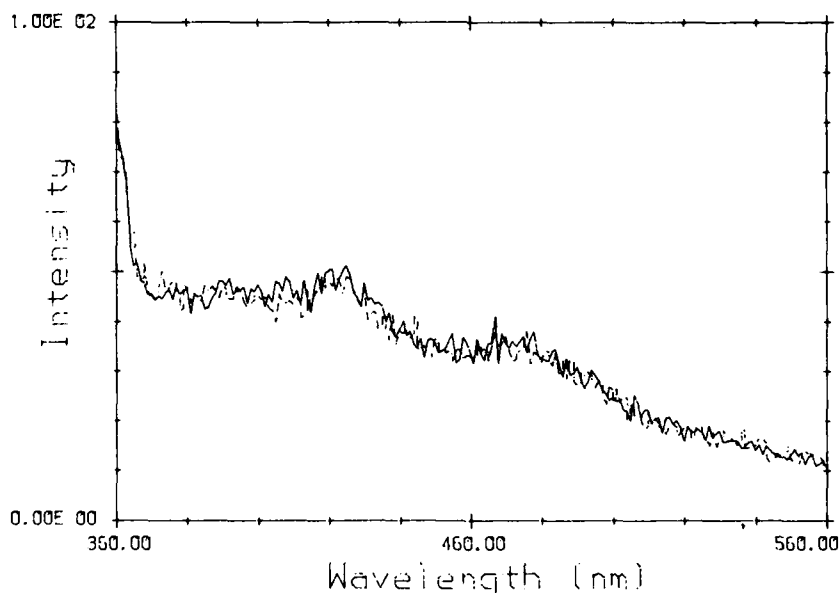


FIGURE 82. Fluorescence Emission Spectrum Started at 1736 on 27 April 1984 During the Incineration of the Yellow XII Smoke. Ex = 344 nm, on-line (—), room air (---). S1/S2 mode. Excitation parameter for anthracene detection.

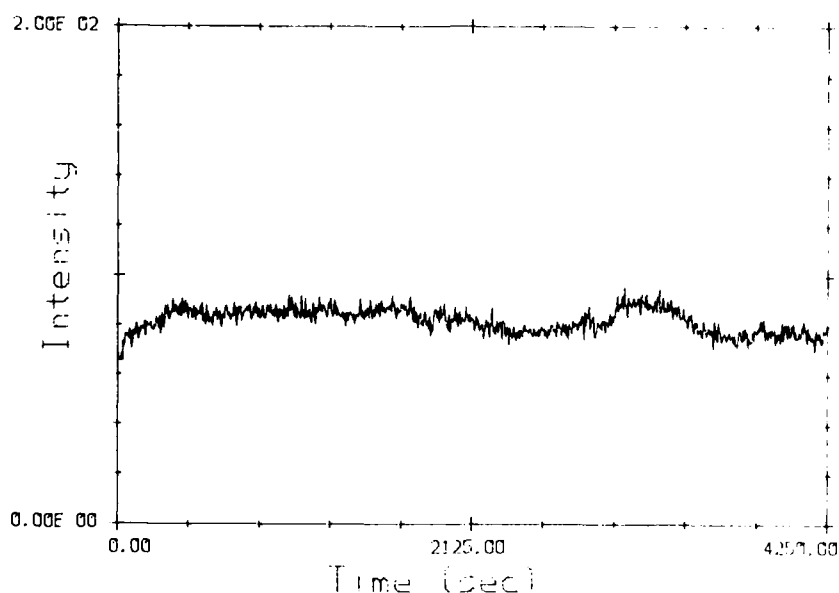


FIGURE 83. Temporal Scan Started at 1933 on 27 April 1984 During the Incineration of the Yellow XII Smoke. Ex = 226 nm, Em = 302 nm, S1/S2 mode. Valves switched off-line to sample room air at 1750 seconds, and back on-line at 2990 seconds.

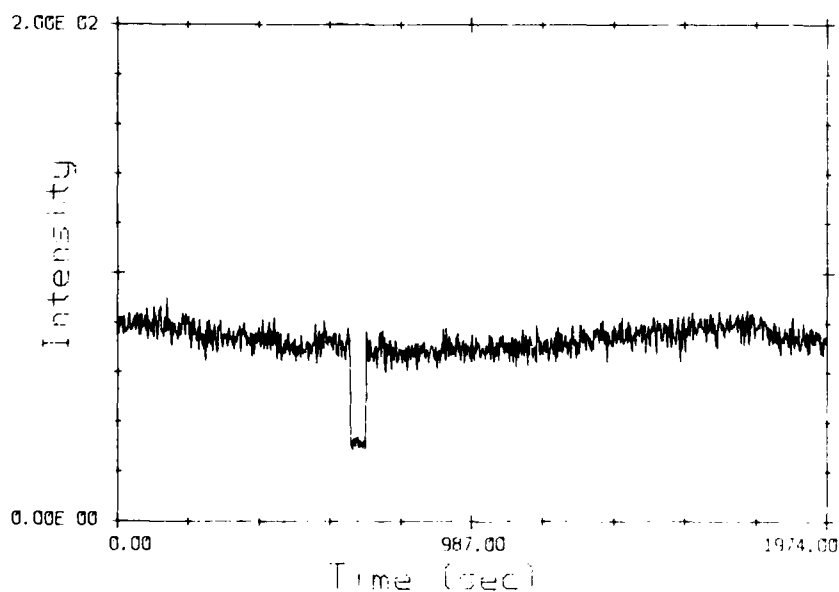


FIGURE 84. Temporal Scan Started at 2052 on 27 April 1984 During the Incineration of the White I Smoke. Ex = 226 nm, Em = 302 nm, S1/S2 mode. Valves switched off-line to sample room air at 1080 seconds, and back on-line at 1455 seconds. The signal decrease near 700 seconds was caused by blocking the photomultiplier to measure the tube dark count.

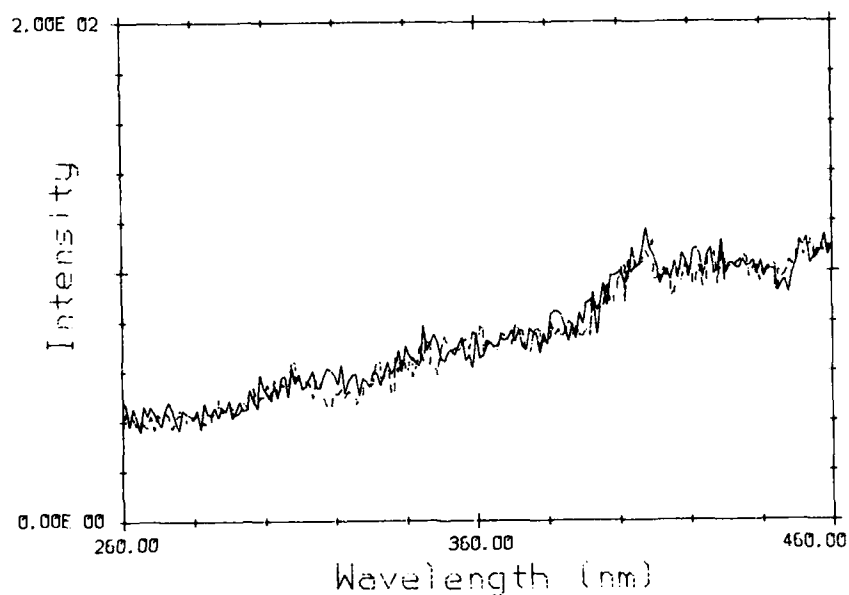


FIGURE 85. Fluorescence Emission Spectrum Started at 2128 on 27 April 1984 During the Incineration of the White I Smoke. Ex = 240 nm, on-line (—), room air (---). S1/S2 mode.

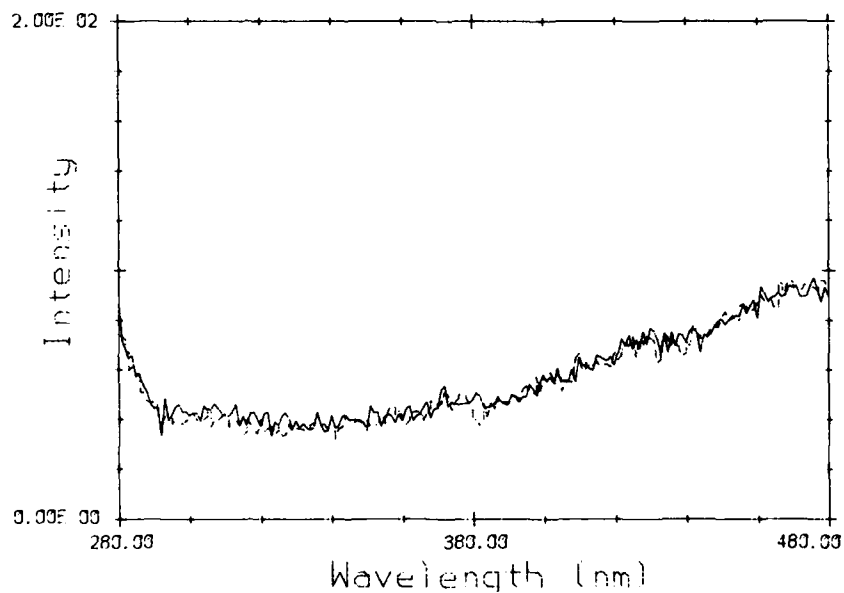


FIGURE 86. Fluorescence Emission Spectrum Started at 2150 on 27 April 1984 During the Incineration of the White I Smoke. Ex = 269 nm, on-line (—), room air (---). S1/S2 mode. Excitation parameter for naphthalene detection.

NWC TP 6559

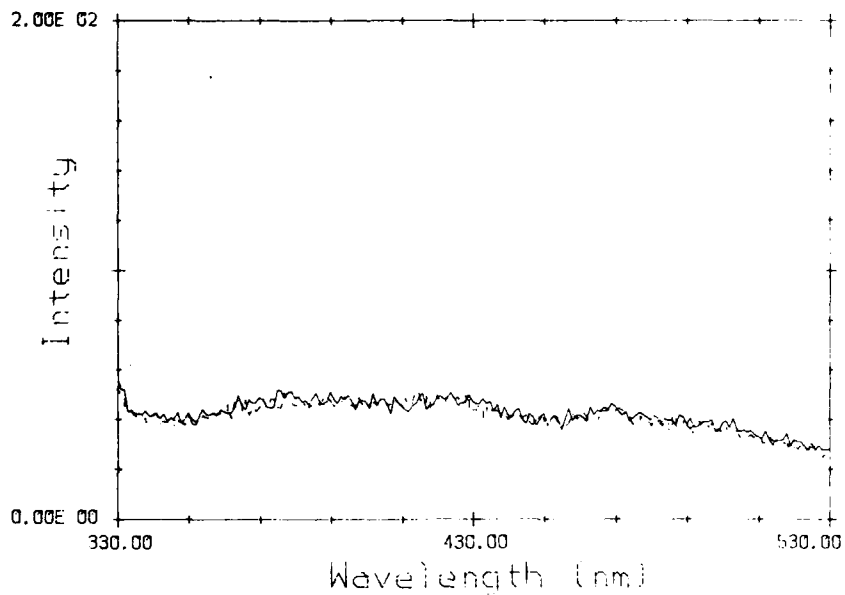


FIGURE 87. Fluorescence Emission Spectrum Started at 2203 on 27 April 1984 During the Incineration of the White I Smoke. Ex = 310 nm, on-line (—), room air (---). S1/S2 mode.

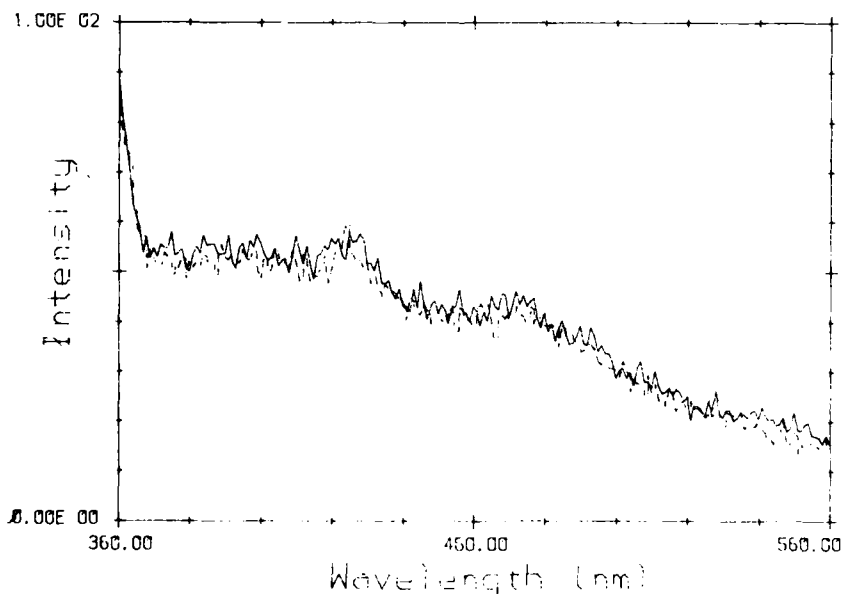


FIGURE 88. Fluorescence Emission Spectrum Started at 2218 on 27 April 1984 During the Incineration of the White I Smoke. Ex = 344 nm, on-line (—), room air (---). S1/S2 mode. Excitation parameter for anthracene detection.

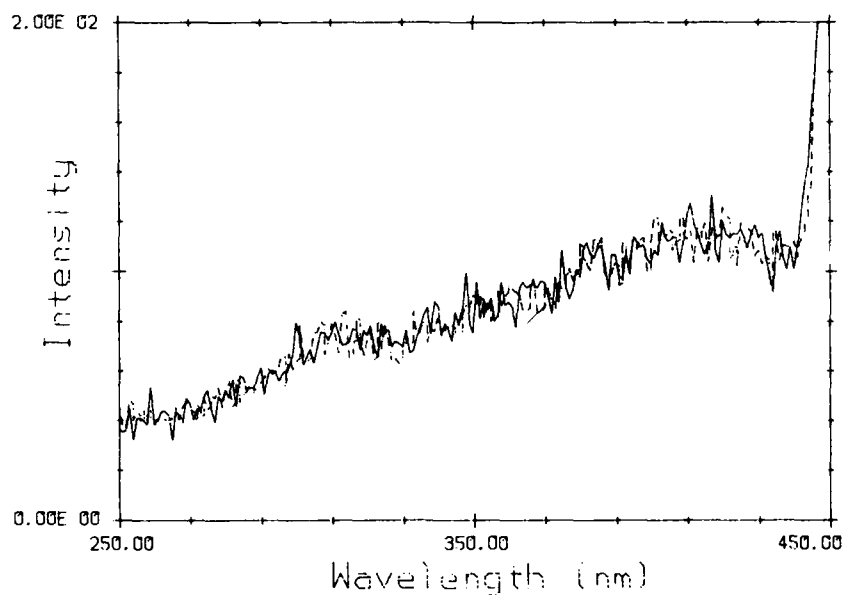


FIGURE 89. Fluorescence Emission Spectrum Started at 2240 on 27 April 1984 During the Incineration of the White I Smoke. Ex = 226 nm, on-line (—), room air (---). S1/S2 mode.

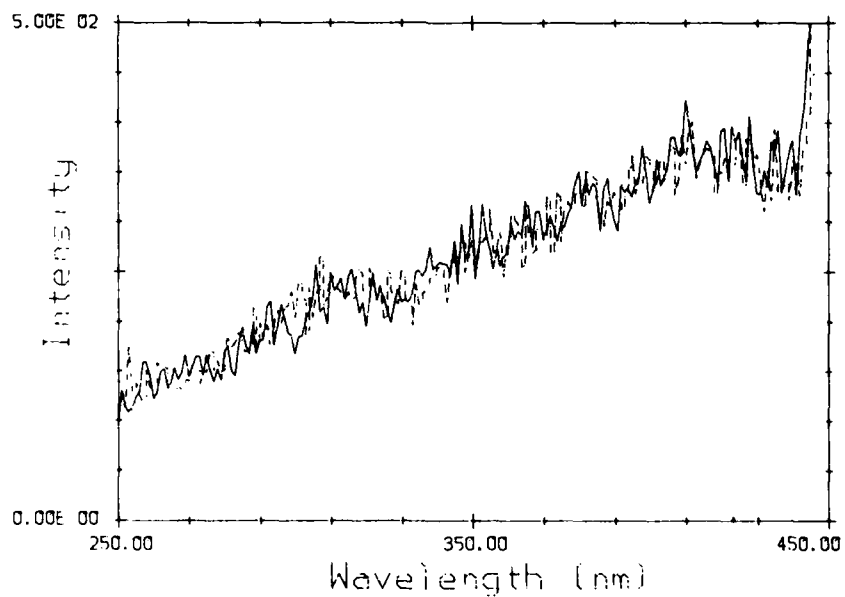


FIGURE 90. Fluorescence Emission Spectrum Started at 2256 on 27 April 1984 During the Incineration of the White I Smoke. Ex = 226 nm, on-line (—), room air (---). S1/S2 mode.

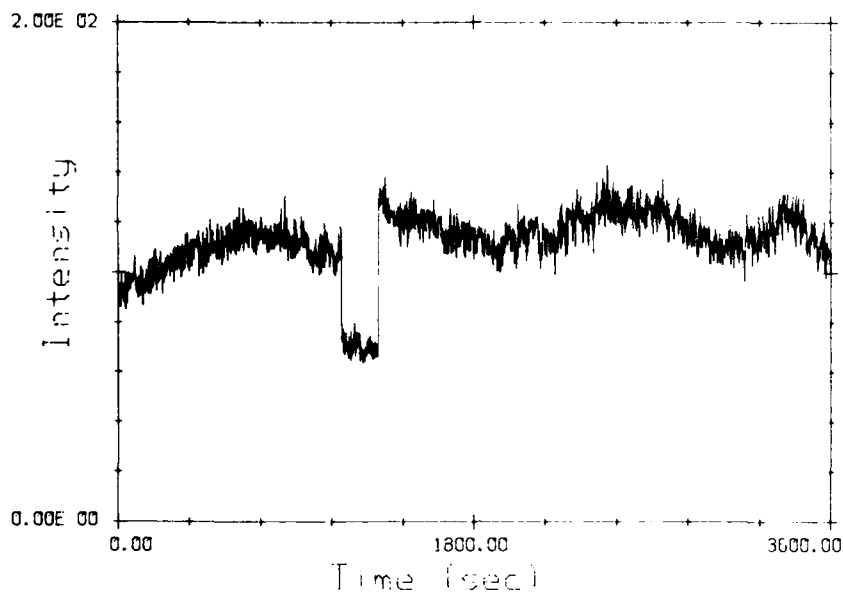


FIGURE 91. Temporal Scan Started at 2330 on 27 April 1984 During the Incineration of the White I Smoke. Ex = 226 nm, Em = 318 nm, S1/S2 mode. Valves switched off-line to sample room air at 1124 seconds, and back on-line at 1314 seconds.

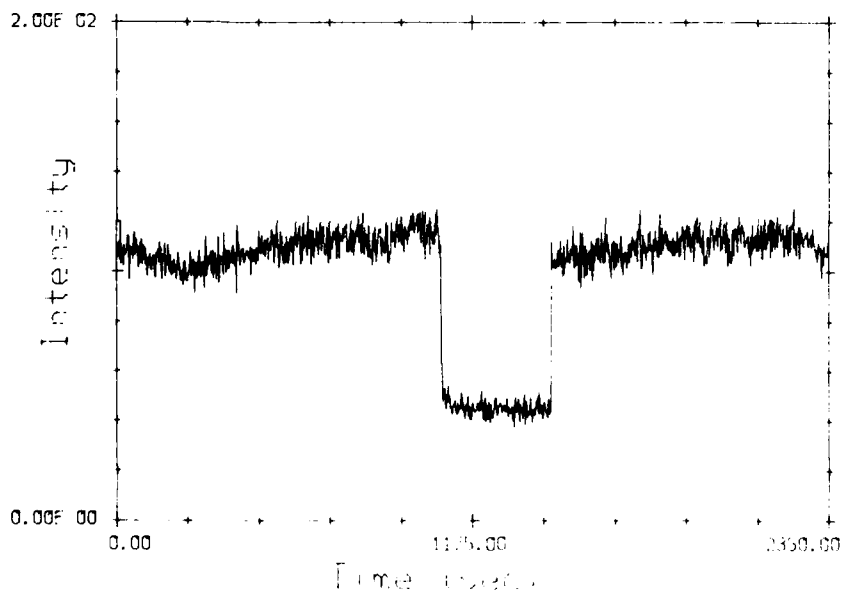


FIGURE 92. Temporal Scan Started at 0038 on 28 April 1984 During the Incineration of the White I Smoke. Ex = 226 nm, Em = 302 nm, S1/S2 mode. Valves switched off-line to sample room air at 1070 seconds, and back on-line at 1440 seconds.

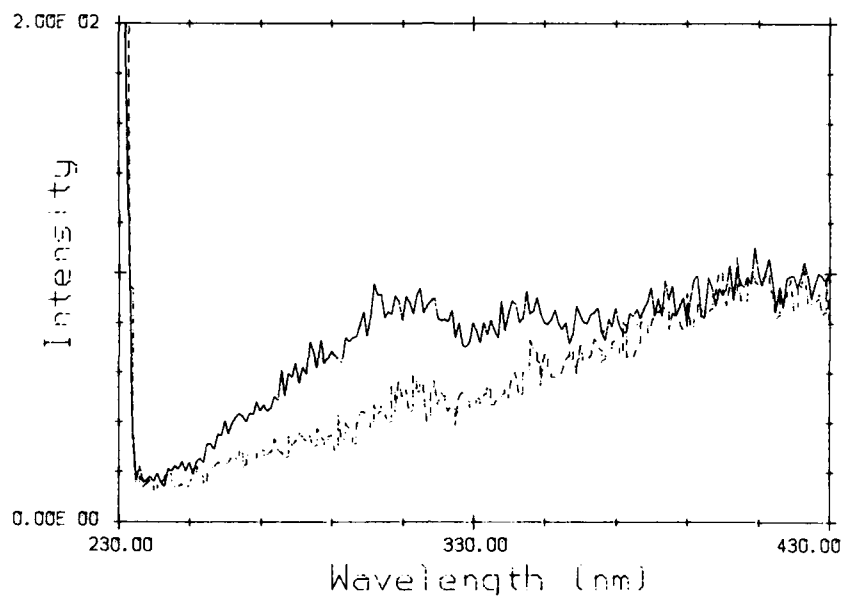


FIGURE 93. Fluorescence Emission Spectrum Started at 0122 on 28 April 1984 During the Incineration of the White I Smoke. Ex = 226 nm, on-line (—), room air (---). S1/S2 mode.

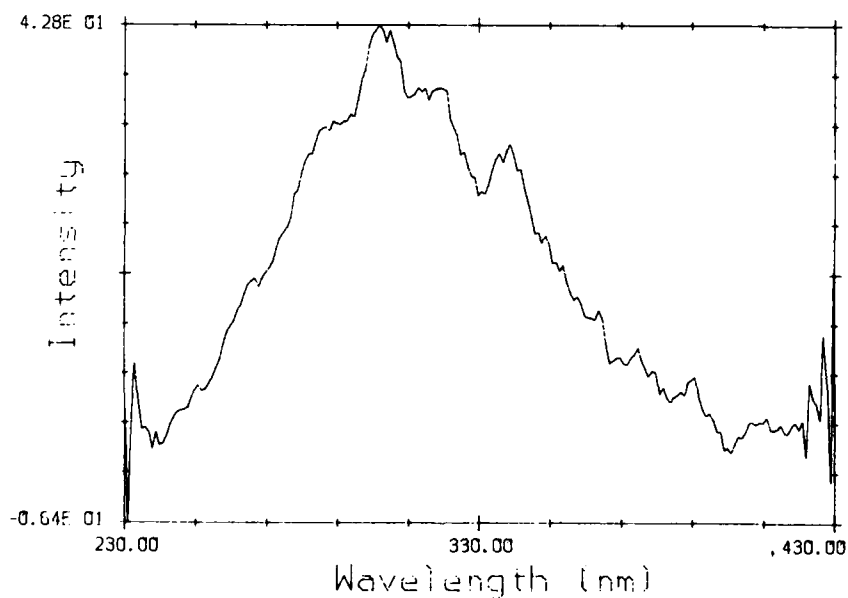


FIGURE 94. Difference Spectrum Obtained by Subtracting the Two Spectra in Figure 93.

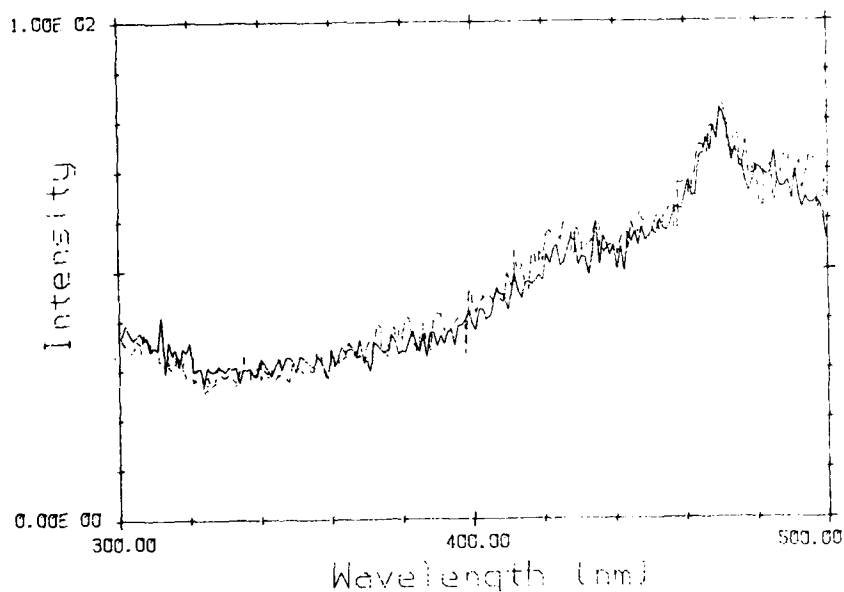


FIGURE 95. Fluorescence Emission Spectrum Started at 0141 on 28 April 1984 During the Incineration of the White I Smoke. Ex = 277 nm, on-line (—), room air (---). S1/S2 mode.

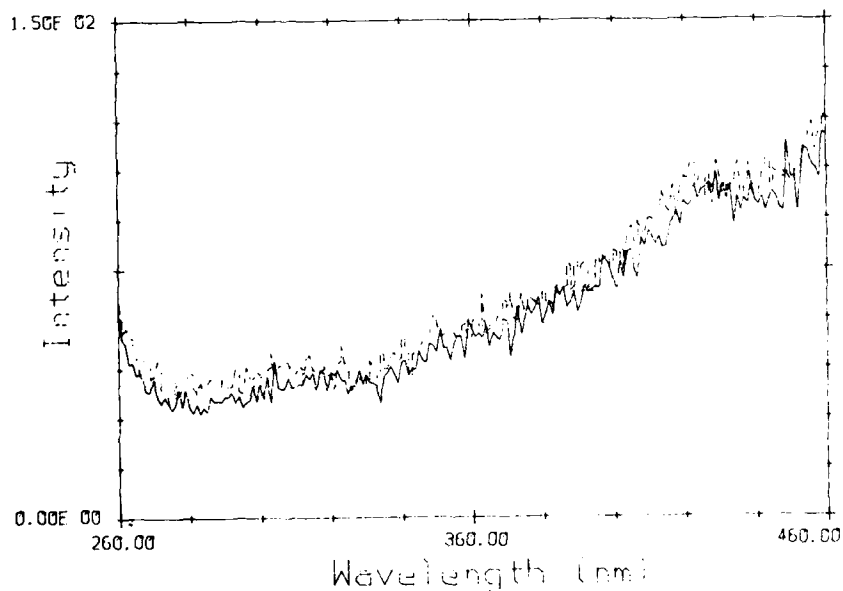


FIGURE 96. Fluorescence Emission Spectrum Started at 0203 on 28 April 1984 During the Incineration of the White I Smoke. Ex = 250 nm, on-line (—), room air (---). S1/S2 mode.

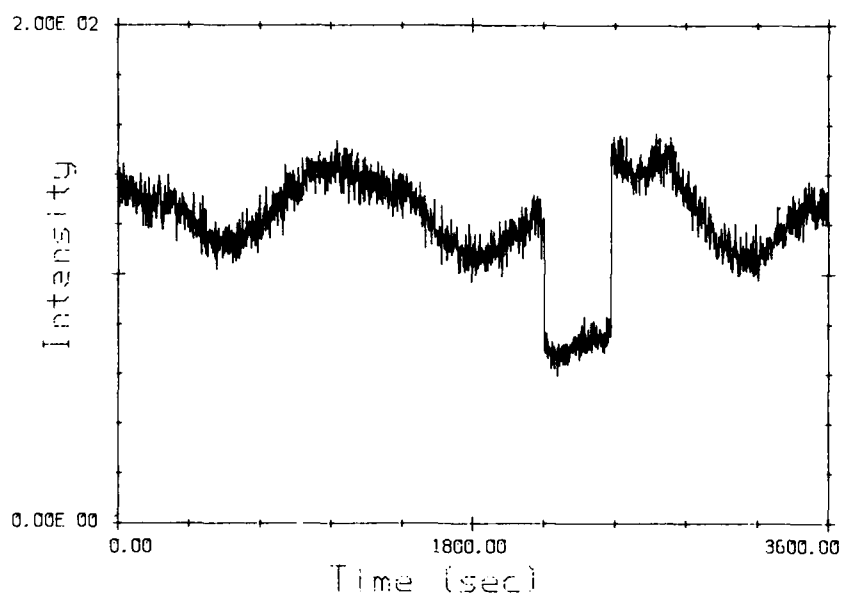


FIGURE 97. Temporal Scan Started at 0220 on 28 April 1984 During the Incineration of the White I Smoke. Ex = 226 nm, Em = 302 nm, S1/S2 mode. Valves switched off-line to sample room air at 2170 seconds, and back on-line at 2500 seconds.

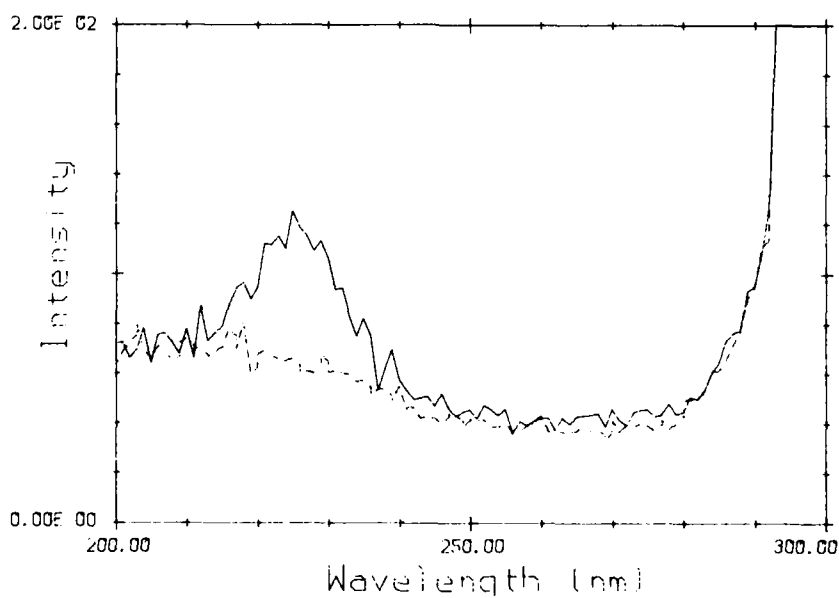


FIGURE 98. Fluorescence Excitation Spectrum Started at 0325 on 28 April 1984 During the Incineration of the White I Smoke. Em = 302 nm, on-line (—), room air (---). S1/S2 mode.

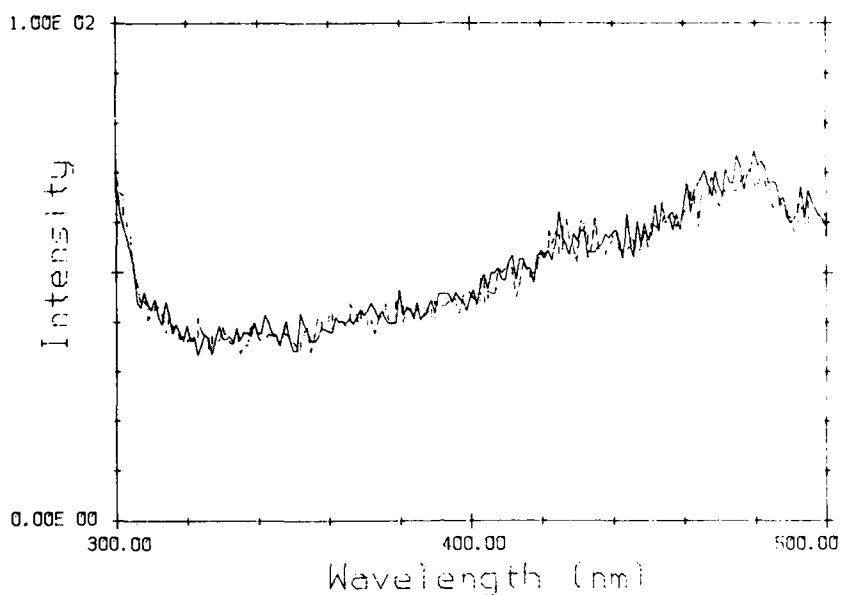


FIGURE 99. Fluorescence Emission Spectrum Started at 0340 on 28 April 1984 During the Incineration of the White I Smoke. Ex = 284 nm, on-line (—), room air (---). S1/S2 mode. Excitation parameter for phenanthrene detection.

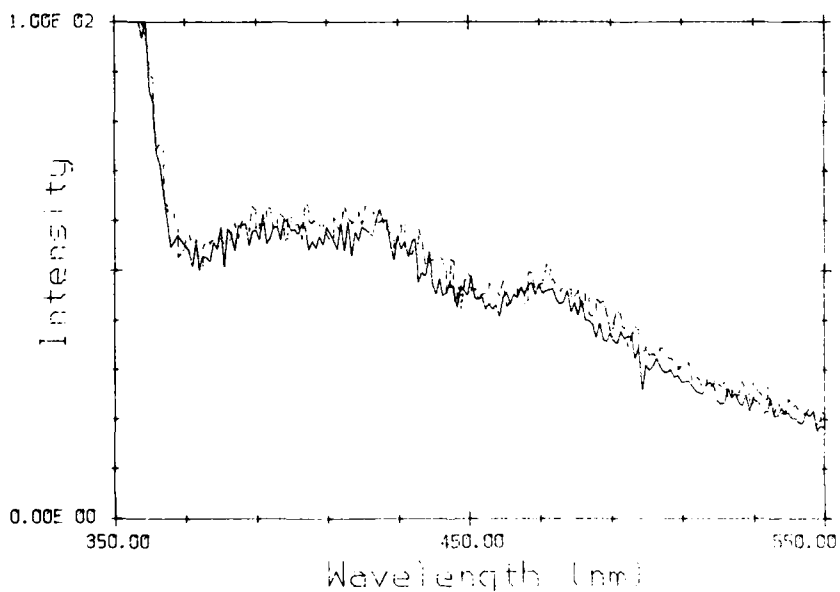


FIGURE 100. Fluorescence Emission Spectrum Started at 0400 on 28 April 1984 During the Incineration of the White I Smoke. Ex = 344 nm, on-line (—), room air (---). S1/S2 mode. Excitation parameter for anthracene detection.

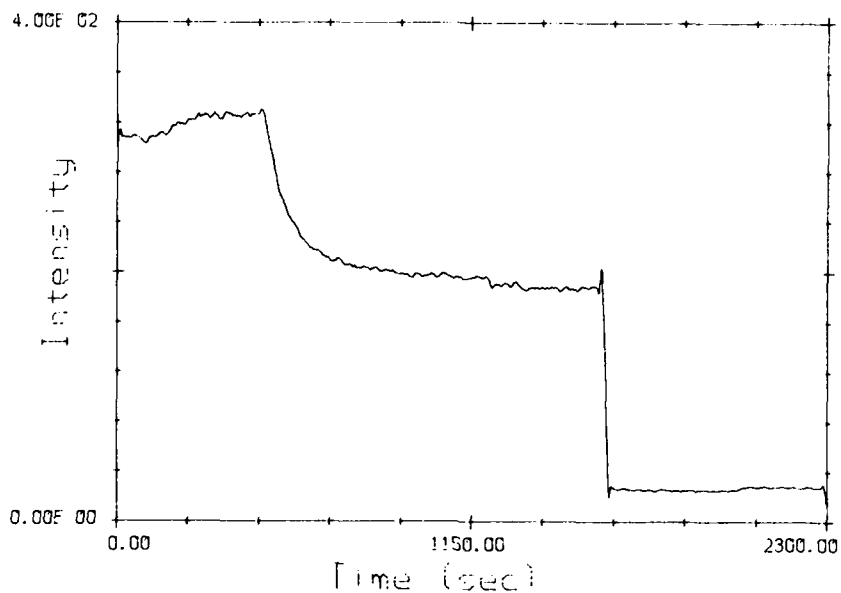


FIGURE 101. Temporal Scan of Naphthalene Calibration. The air flowrate was changed from 80 to 160 mL/min at 450 seconds and to a room air flow at 1595 seconds. The naphthalene concentrations would be 12.4, 6.2, and 0.0 ppm, respectively.

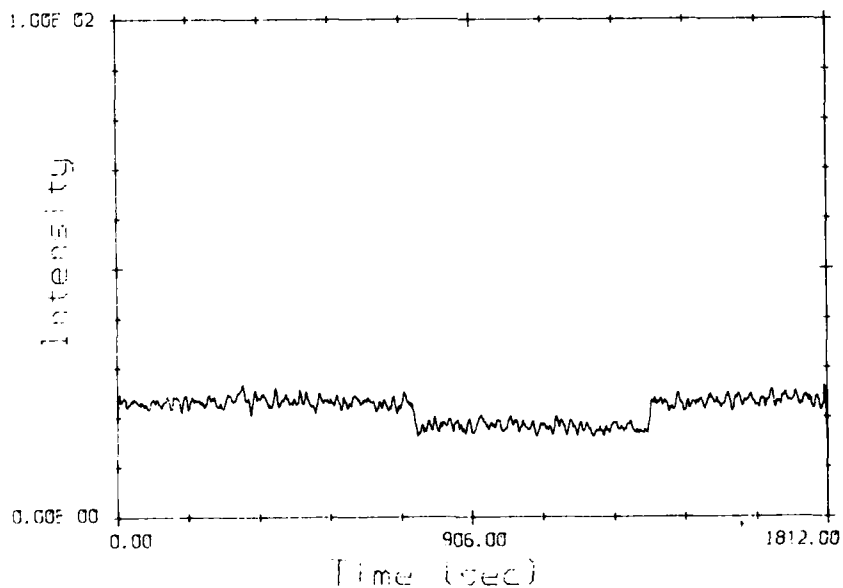


FIGURE 102. Temporal Scan Started at 1117 on 28 April 1984 During the Incineration of Gas Only. Ex = 226 nm, Em = 260 nm, S1/S2 mode. Valves switched off-line to sample room air at 770 seconds, and back on-line at 1358 seconds. Wavelength parameters selected for NO detection.

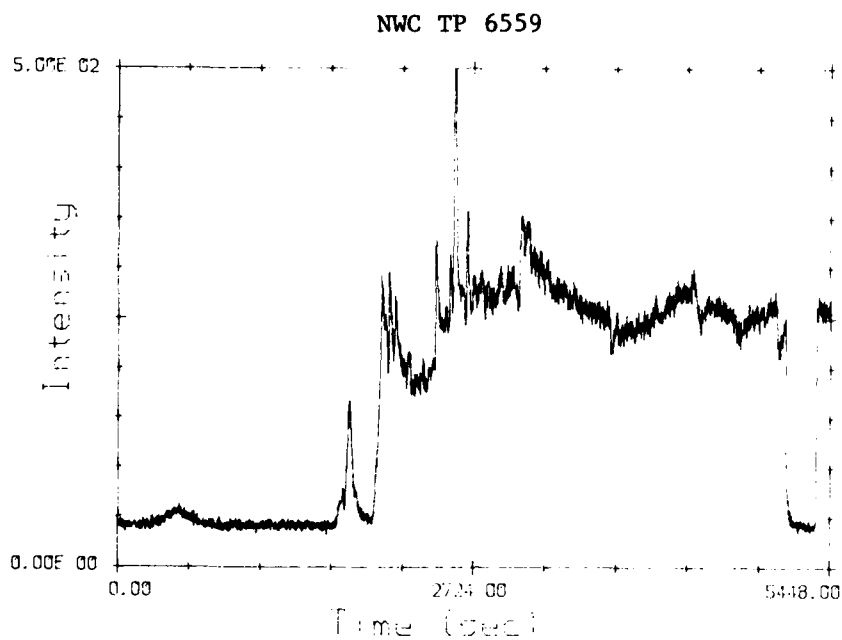


FIGURE 103. Temporal Scan Started at 1316 on 28 April 1984 During the Incineration of the Smoke Formulation mixture. Ex = 226 nm, Em = 302 nm, S1/S2 mode. Valves switched off-line to sample room air at 5105 seconds, and back on-line at 5350 seconds.

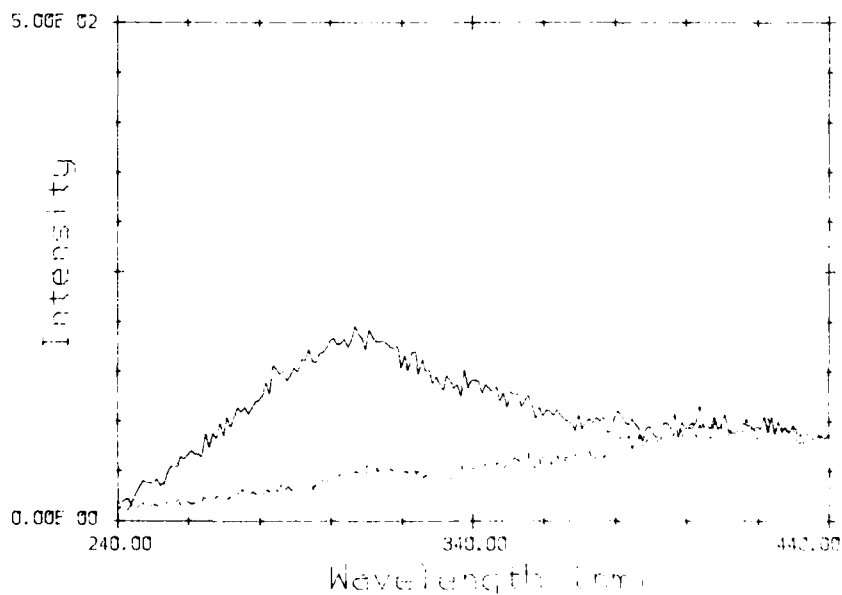


FIGURE 104. Fluorescence Emission Spectrum Started at 1452 on 28 April 1984 During the Incineration of the Smoke Formulation Mixture. Ex = 226 nm, on-line (—), room air (---). S1/S2 mode.

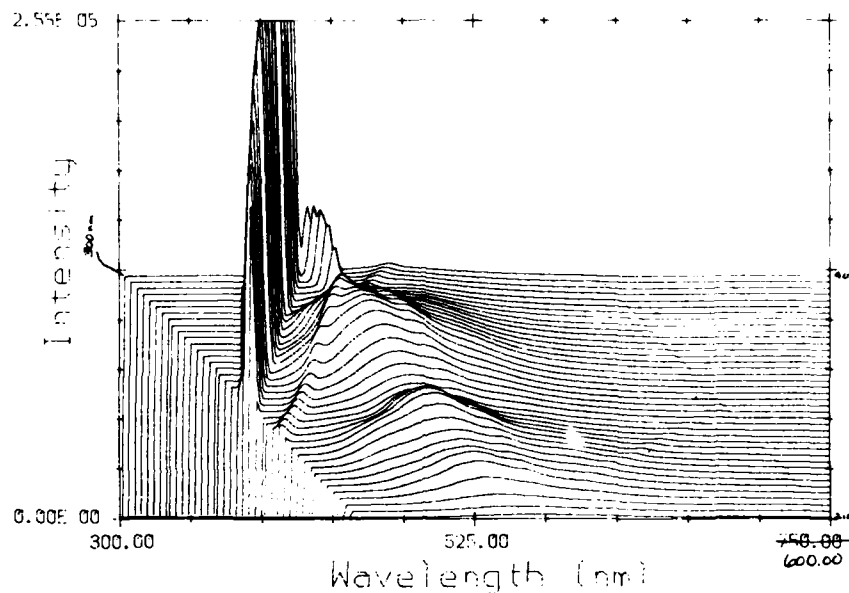


FIGURE 105. Excitation-Emission Matrix Generated from the Quench Sump Water in a 1 cm Cuvette. QS sample #17, 26 April 1984, 0315, POST 03 P1. Excitation values were incremented in 5 nm steps from 210-405 nm. The emission was scanned from 300-600 nm, in 1 nm steps. S1/S2 mode. The program used was from Spex Technical Note #62.

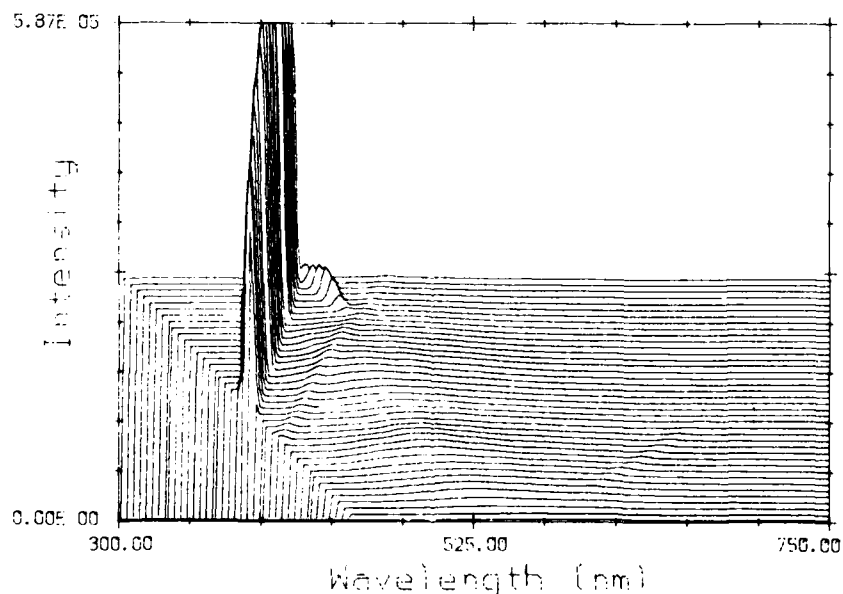


FIGURE 106. Excitation-Emission Matrix Generated from the Absorber Tower Sump Water in a 1 cm Cuvette. ATS sample #17, 26 April 1984, 1240. Excitation values were incremented in 5 nm steps from 210-405 nm. The emission was scanned from 300-600 nm, in 1 nm steps. S1/S2 mode. The program used was from Spex Technical Note #62.

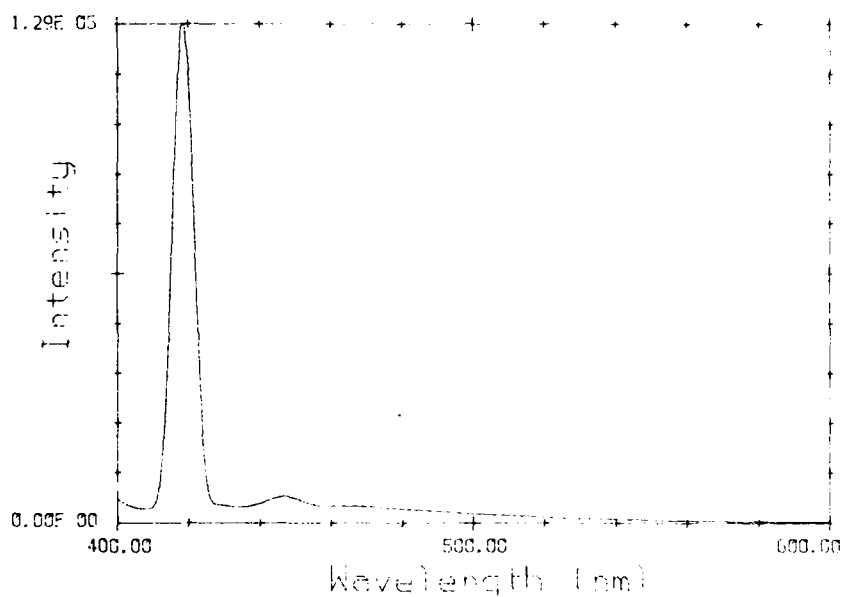


FIGURE 107. Selective Fluorescence Emission Spectrum of the Pump Trap Water in a 1 cm Cuvette. Ex = 388 nm, S1/S2 mode.

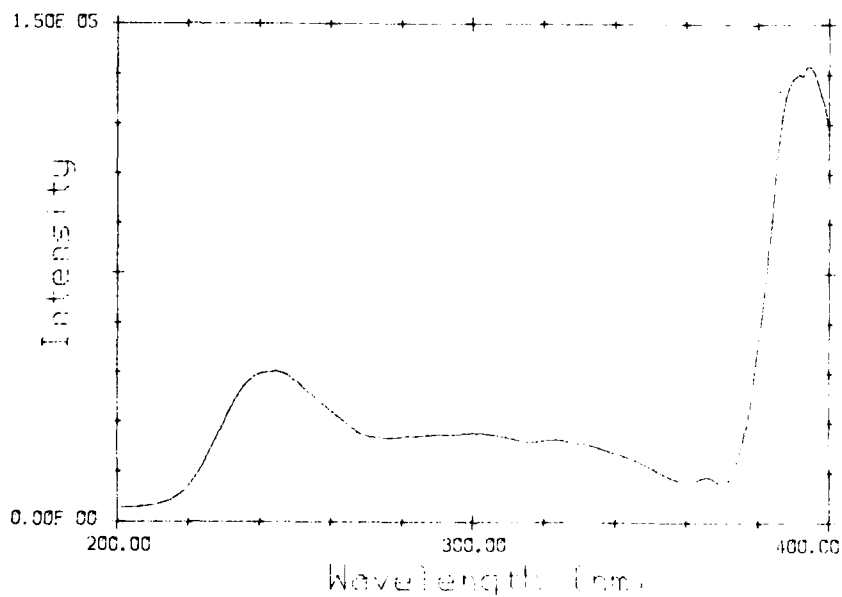


FIGURE 108. Selective Fluorescence Excitation Spectrum of the Pump Trap Water in a 1 cm Cuvette. Em = 419 nm, S1/S2 mode.

NWC TP 6559

Appendix A

**INGREDIENTS AND SPECIFICATIONS OF ARMY
COLORED SMOKE COMPOSITIONS**

NOTES

REVISIONS

REV	DATE	DESCRIPTION
1	10/1/61	REPLACES B143-3-1 REV D, E, F, G
2	10/1/61	185-6 AND 185-7 (1) INC.
3	10/1/61	10155-19 INC
4	10/1/61	10155-42 INC
5	10/1/61	INC NOR 155-013C1-003
6	10/1/61	INC NOR 155-048-013

ITEM	PARTICLE SIZE 1/ PERCENT PASSING MINIMUM NO. 30	PERCENT PASSING MINIMUM NO. 100	PERCENT PASSING MINIMUM NO. 200	PERCENT PASSING MINIMUM NO. 400	PARTS BY WEIGHT
Dye, Red	97	90	70		40 ± 1.0
MIL-D-3718					
Sodium Bicarbonate		99	80 Max		25 ± 2.0
O-B-376					
Potassium Chlorate	99	90	60		36 ± 2.0
MIL-P-130					
Grade B, Class 7					
Sulphur		99	85 Min		9 ± 1.0
MIL-S-487					
Grade E					

NOTES:

- AN ALTERNATE METHOD FOR GRANULATING THE PYROPHOR WITH ACETONE MAY BE USED. IF ACETONE IS USED, KEROSENE IS NOT TO BE ADDED.

NOTES:

- THIS DRAWING SHALL BE INTERPRETED IN ACCORDANCE WITH APPLICABLE STANDARDS LISTED IN MIL SPEC MA-D1000
- THE FOLLOWING ARE MANDATORY WHEN INDICATED BY B
 - REMOVE BURRS
 - BREAK SHARP EDGES .010 MAX
 - FILETS .010 MAX R.
 - ALL OVER, EXCEPT AS NOTED
 - DIMENSIONS APPLY AFTER PLATING
 - TOLERANCES ON STOCK MATERIAL SIZES, SHALL BE AS SPECIFIED IN APPLICABLE SPECIFICATIONS.
- Water-soluble barium (W-E-280), in a quantity not exceeding 4 percent of the dye content, may be blended instantaneously with the smoke mixture to prevent dusting.
- Tricalcium phosphate, in a quantity not exceeding 0.38 percent of the weight of potassium chlorate, may be mixed intimately with potassium chlorate to prevent caking.

REVISIONS

REV	DATE	DESCRIPTION
1	10/1/61	REPLACES B143-3-1 REV D, E, F, G
2	10/1/61	185-6 AND 185-7 (1) INC.
3	10/1/61	10155-19 INC
4	10/1/61	10155-42 INC
5	10/1/61	INC NOR 155-013C1-003
6	10/1/61	INC NOR 155-048-013

REVISIONS

REV	DATE	DESCRIPTION
1	10/1/61	REPLACES B143-3-1 REV D, E, F, G
2	10/1/61	185-6 AND 185-7 (1) INC.
3	10/1/61	10155-19 INC
4	10/1/61	10155-42 INC
5	10/1/61	INC NOR 155-013C1-003
6	10/1/61	INC NOR 155-048-013

REVISIONS

REV	DATE	DESCRIPTION
1	10/1/61	REPLACES B143-3-1 REV D, E, F, G
2	10/1/61	185-6 AND 185-7 (1) INC.
3	10/1/61	10155-19 INC
4	10/1/61	10155-42 INC
5	10/1/61	INC NOR 155-013C1-003
6	10/1/61	INC NOR 155-048-013

REVISIONS

REV	DATE	DESCRIPTION
1	10/1/61	REPLACES B143-3-1 REV D, E, F, G
2	10/1/61	185-6 AND 185-7 (1) INC.
3	10/1/61	10155-19 INC
4	10/1/61	10155-42 INC
5	10/1/61	INC NOR 155-013C1-003
6	10/1/61	INC NOR 155-048-013

REVISIONS

REV	DATE	DESCRIPTION
1	10/1/61	REPLACES B143-3-1 REV D, E, F, G
2	10/1/61	185-6 AND 185-7 (1) INC.
3	10/1/61	10155-19 INC
4	10/1/61	10155-42 INC
5	10/1/61	INC NOR 155-013C1-003
6	10/1/61	INC NOR 155-048-013

REVISIONS

REV	DATE	DESCRIPTION
1	10/1/61	REPLACES B143-3-1 REV D, E, F, G
2	10/1/61	185-6 AND 185-7 (1) INC.
3	10/1/61	10155-19 INC
4	10/1/61	10155-42 INC
5	10/1/61	INC NOR 155-013C1-003
6	10/1/61	INC NOR 155-048-013

REVISIONS

REV	DATE	DESCRIPTION
1	10/1/61	REPLACES B143-3-1 REV D, E, F, G
2	10/1/61	185-6 AND 185-7 (1) INC.
3	10/1/61	10155-19 INC
4	10/1/61	10155-42 INC
5	10/1/61	INC NOR 155-013C1-003
6	10/1/61	INC NOR 155-048-013

REVISIONS

REV	DATE	DESCRIPTION
1		

1/ PARTICLE SIZE SHALL BE AS PRESCRIBED IN THIS TABLE PRIOR TO MIXING. WHEN PARTICLE SIZE DESIGNATED IN THE SPECIFICATION DOES NOT CONFORM TO THE TABLE, SUBJECT MATERIAL SHALL BE PROCESSED TO CONFORM TO THIS TABLE.

REVISIONS		DATE		BY	
LINE	DESCRIPTION	DATE	BY	DATE	BY
D	REPLACES B143-4-1, RTT C: S.O.	5/8/67			
E	155-8 AND S.O. 751-1, INC.	5/8/67			
F	EO 155-19 INC	5/8/67			
G	EO 155-42 INC	5/8/67			
H	NOR 155-016-003 INC	5/8/67			
I	INC NOR 155-032C-002	5/8/67			
J	INC NOR 155-048-013 AND SPEC MIL-D-0050074 HAS MIL-D-50074.	5/8/67			

Ingredient and Specification	Particle Size 1/ Percent Passing Blafum B1-E-368					Parts by Weight
	840 (20)	297 (80)	177 (100)	74 (200)	44 (325)	
Dye, Yellow MIL-D-0050029	100	97				14.0 ± 0.5
Benzothione MIL-D-0050074	100	97				24.5 ± 1.0
Sulphur MIL-B-487 Grade E			99	95	95	8.5 ± 1.0
Potassium Chlorate MIL-B-130 Grade B, Class 7			99	90	60	20.0 ± 2.0
Sodium Bicarbonate O-B-378				99	90	33.0 ± 2.0

NOTES:

1. AN ALTERNATE METHOD FOR GRANULATING THE PYROMIX WITH ACETONE MAY BE USED. IF ACETONE IS USED KEROSENE IS NOT TO BE ADDED.

2. THE FOLLOWING ARE MANDATORY WHEN INDICATED BY B

3. REMOVE BURRS □ BREAK SHARP EDGES .010 MAX

4. PALLETS .910 MAX R.

5. □ ALL OVER, EXCEPT AS NOTED

6. DIMENSIONS APPLY AFTER PLATING

7. TOLERANCES ON STOCK MATERIAL SIZE SHALL BE AS SPECIFIED IN APPLICABLE SPECIFICATIONS.

8. Water-white benzene (77-8-239), in a quantity not exceeding 10 percent of the dye content, may be blended intimately with make mixture to prevent dusting.

9. Tricelcic phosphate, in a quantity not exceeding 0.20 percent of the weight of potassium chlorate, may be sized intimately with potassium chlorate to prevent caking.

1/ Particle size shall be as prescribed in this table prior to mixing. When particle size designated in the specification does not conform to the table, subject material shall be processed to conform to this table.

1

SYSTEMS									
ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS	DATE	BY	REVISION	REMARKS
A	GENERAL CHANGE								
B	(1) MIL-8-335, 8155 60, 100, AND 200 CHANGED, (2) ADDED COIS 151, 150 NEXT ASST C114-1-21 AND NEXT ASST 83D10106 AND NEXT ASST C114-1-75, MIL-8-335 WAS 104 MAX, 90.8 MIN; 88.6 MAX 88.6 MIN, 23.2 MAX 17.2 MIN								
C	(1) REMOVED AIR FORCE DRG -- (2) ADDED C14-5-2523								
D	NEXT ASST								
E	INC NGR 144-014-002								
F	ADDED N/A D15 11-21B AND COUE NO 110								
G	NOR 147-277 COI INC								
H	ADDED N/A D36-1-26 AND COUE NO 147 INC NGR 144-032-001								
J	ADDED NEXT ASSEMBLY "E36-1-18" AND EIC NO. 871								

Ingredient and Specification	Particle Size 1/ 32-2-248		Parts by Weight
	840 (20)	149 (100)	
Hexachlorothane MIL-8-335	98Min 50Min 30Max	10Max 44.53 ± 0.50	
Zinc Oxide MIL-8-335	100 97	99.9 99.0	46.47 ± 0.50
Aluminum Chloride MIL-8-335			80 87 87 Max
Type 11, Grade C, Class 4			

NOTE: 1. The mixture shall be prepared in accordance with the following instructions: a. The mixture shall be prepared in a clean, dry container. b. The mixture shall be prepared in a clean, dry container. c. The mixture shall be prepared in a clean, dry container.

2. The ingredients are blended into a homogeneous mixture with no lumps or agglomeration.

3. Protect both the ingredients and the mixture from absorption of atmospheric moisture during overnight storage.

4. Burning Time. The mixture shall meet the burning time specified in the applicable and item specification. During time shall be changed by adjusting the aluminum content but in no case will the ratio of hexachlorothane and zinc oxide be altered.

5. MOISTURE CONTENT OF FINAL MIXTURE EXCEED 0.25 PERCENT

6. ALL INGREDIENTS SHALL MEET SPECIFICATION REQUIREMENTS PRIOR TO MIXTURE LOADING

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
E36-1-18					
D36-1-26					
C114-1-75					
C14-5-2523					
D15-11-21B					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

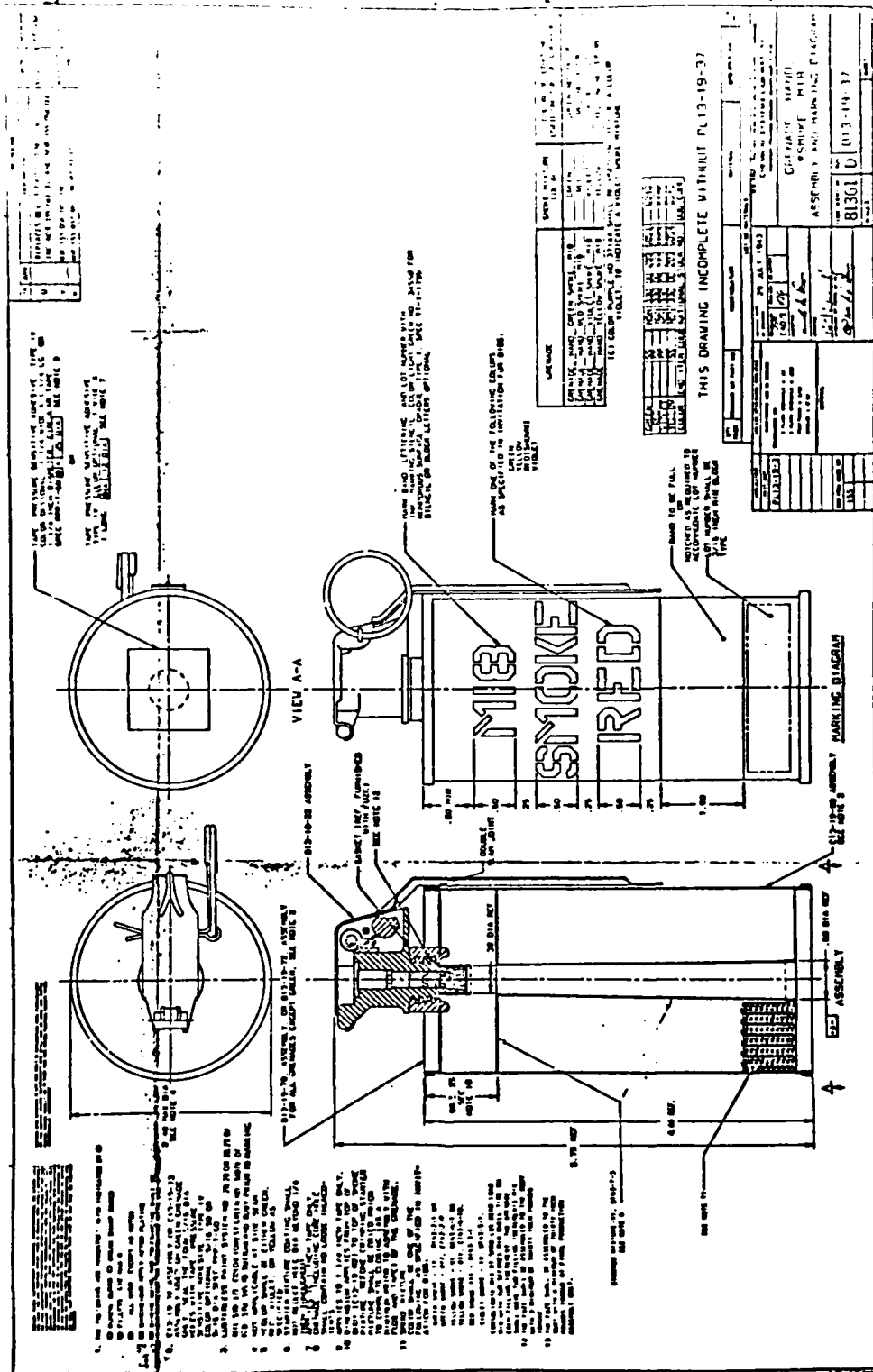
ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					
139					
130					

ITEM	DESCRIPTION	DATE	BY	REVISION	REMARKS
147					
840					
161					
144					
140					



INITIAL DISTRIBUTION

- 9 Naval Air Systems Command
 - AIR-03B, H. Andrews (1)
 - AIR-03D, G. Heiche (1)
 - AIR-310G, R. Shumaker (1)
 - AIR-320R, H. Rosenwasser (1)
 - AIR-330 (1)
 - AIR-35 (1)
 - AIR-536A1 (1)
 - AIR-7226 (2)
- 5 Chief of Naval Operations
 - OP-225 (1)
 - OP-354 (1)
 - OP-506 (1)
 - OP-982E (1)
 - OP-982F (1)
- 1 Chief of Naval Material (MAT-08)
- 5 Chief of Naval Research, Arlington
 - ONR-440 (1)
 - ONR-443 (1)
 - ONR-460 (1)
 - ONR-470 (1)
 - ONR-472 (1)
- 3 Naval Facilities Engineering Command, Alexandria
 - Code 032, S. Hurley (1)
 - Code 112 (1)
 - Code 54 (1)
- 7 Naval Sea Systems Command
 - SEA-04E (1)
 - SEA-05R1 (1)
 - SEA-05R14 (1)
 - SEA-05R16 (1)
 - SEA-09B312 (2)
 - SEA-62R32 (1)
- 1 Commander in Chief, U.S. Pacific Fleet (Code 325)
- 1 Commander, Third Fleet, Pearl Harbor
- 1 Commander, Seventh Fleet, San Francisco
- 2 Naval Academy, Annapolis (Director of Research)
- 2 Naval Air Development Center, Warminster
 - Library (1)
- 1 Naval Air Propulsion Center, Trenton (PE-71, A. F. Klarman)
- 1 Naval Energy and Environmental Support Activity, Port Hueneme
- 3 Naval Ocean Systems Center, San Diego
 - Code 521, M. H. Salazar (1)
 - Code 522
 - S. Yamamoto (1)
 - A. Zirino (1)
- 2 Naval Ordnance Station, Indian Head
 - Code E, Pollution Abatement Program Manager (1)
 - Technical Library (1)

- 3 Naval Research Laboratory
 - Code 4300 (1)
 - Code 6100 (1)
 - Library (1)
- 3 Naval Ship Weapon Systems Engineering Station, Port Hueneme
 - Code 5711, Repository (2)
 - Code 5712 (1)
- 2 Naval Surface Weapons Center, Dahlgren
 - G51 (1)
 - Technical Library (1)
- 5 Naval Surface Weapons Center, White Oak Laboratory, Silver Spring
 - Code R11 (2)
 - Code R16, J. Hoffsommer (1)
 - Code R17 (1)
 - Code R141, G. Young (1)
- 1 Naval Underwater Systems Center, Newport (Code 364, R. Kronk)
- 1 Naval War College, Newport
- 6 Naval Weapons Support Center, Crane
 - Code 3025, D. Burch (1)
 - Code 50C, B. E. Douda (1)
 - Code 505, J. E. Short (1)
 - NAPEC (1)
 - R&E Library (2)
- 4 Office of Naval Technology, Arlington
 - MAT-0716 (1)
 - MAT-072 (1)
 - MAT-0723 (1)
 - MAT-0724 (1)
- 1 Army Armament Munitions & Chemical Command, Rock Island (DRSMC-DSM-D(R), G. T. Zajicek)
- 1 Army Environmental Hygiene Agency, Aberdeen Proving Ground (HSHB-EA-A)
- 1 Army Medical Bioengineering Research and Development Laboratory, Fort Dietrick (J. Barkeley)
- 1 Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground (DRXTH-TE-D)
- 3 Air Force Systems Command, Andrews Air Force Base
 - DLFP (1)
 - DLWA (1)
 - SDZ (1)
- 1 Air Force Armament Division, Eglin Air Force Base (AFATL/DLJW, D. Harrison)
- 1 Air Force Intelligence Service, Bolling Air Force Base (AFIS/INTAW, Maj. R. Lecklider)
- 12 Defense Technical Information Center
 - 1 Los Alamos National Laboratory, Los Alamos, NM (R. Koenig, MS E517)
 - 1 Michigan State University, East Lansing, MI (Chemistry Department, E. D. Erickson)
 - 3 The Johns Hopkins University, Applied Physics Laboratory, Chemical Propulsion Information Agency, Laurel, MD
 - T. W. Christian (2)
 - J. Hannum (1)

END

FILMED

5-85

DTIC